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CONTINUED STUDY
OF
SEDIMENTS FROM THE SUSQUEHANNA RIVER BASIN IN NEW YORK
WITH EMPHASIS ON
SURFICIAL HEAVY METAL CONTENT

Final Report on Susquehanna
River Basin Commission Project
No. 97 (RF/SUNY NO. 40-6029B)

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by

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ABSTRACT

Bottom sediments from the Susquehanna River Basin in New York State have been analyzed for the surficial concentrations of eleven heavy metals, and characterized as to size distribution, mineralogy, cation exchange capacity (CEC), phosphorus content and total organic carbon. Typical downstream sediments are 76% sand*, 23% silt, and 1% clay, the latter containing illite and some chlorite. The average element concentrations range from 0.012 µg/g for Hg to 12.6 mg/g for Fe, the order of concentrations generally being Hg << As ≅ Cd < Ag ≅ Cr < Cu ≅ Ni ≅ Pb < Zn < P ≅ Mn << C < Fe. Intensive sampling in 1975 at 22 sites downstream from the Binghamton, N.Y. area documented the extent of urban pollution in the elements Ag, Cd, Cu, and Hg. This was evident also on comparing the sediments before and after Tropical Storm Eloise; the concentrations of Ag, Cd, Cu, Hg, Ni, Pb, and Zn were lower after the storm in all three size fractions, suggesting that the near-flood waters scoured the channel and brought in fresh, cleaner sediments. A survey of the Tioga River sub-basin showed that acid mine drainage was probably the source of high Ni and Zn concentrations in sediments from that area. Detailed analysis of sand, silt, and clay fractions revealed the tendency of element concentrations and CEC to increase with decreasing particle size. Average concentration ratios in sand/silt/clay have been established for all the elements, the median ratios being 1/2.2/7.9. The corresponding CEC ratios were 1/1.7/3.9, explaining some (but not all) of the element increases. Humic acids represented only about 5% of the total organic matter in sediments. Linear regression analysis revealed some strong

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*USGS basis (see Note, p. 2)

element-element correlations among pollutant trace metals, but correlations were weak between organic carbon, Fe, or Mn and most metals, especially within a given size fraction. These data, and experiments on the uptake and release of Cd(II) and Pb(II) by sediment materials, provide insight on the mechanism of heavy metal transport, especially pollutant metals, in rivers such as the Susquehanna. Calculations of the annual transport of heavy metals from the New York Susquehanna basin into Pennsylvania show that the dissolved load accounts for 28 to 50% of the transport, the clay fraction carries 28 to 44%, silt carries 13 to 26%, and sand only 2% or less. Comparisons with data from other river systems show more similarities than differences, and the transport load of the Susquehanna on a unit area basis may rival that of the Rhine River for several trace metals.

I. INTRODUCTION

This report describes results obtained from February 1975 through June 1976 in the characterization and analysis of bottom sediments from the Susquehanna River Basin in New York, with some samples from the Tioga River sub-basin in Pennsylvania. The work represents a follow-up of the 1974-75 report, "Preliminary Study of Sediments from the Susquehanna River Basin in New York with Emphasis on Surficial Heavy Metal Content," (1) in which base-line data for the Chemung and Upper Susquehanna sub-basins were established and elevated concentrations of several heavy metals (HM's) were found in Susquehanna River sediments downstream from the Binghamton, N.Y. area.

In July 1975, to further assess HM concentrations and pollution downstream from Binghamton, an intensive series of 22 samples were collected in a 30-mile stretch of the Susquehanna River from Johnson City, N.Y., to the Pennsylvania State Line. Then in November 1975, eight weeks after the near-flood conditions of Tropical Storm Eloise, four of these sites were resampled, along with the upstream sites at Conklin and Chenango Bridge sampled in 1974. Results on the HM concentrations in these samples, along with data from the 1974 samplings, provide the basis for interesting spatial and temporal comparisons. Also, to investigate the source of high Ni and Zn found in 1974 at Gang Mills on the Tioga River, five sites in the Tioga sub-basin were sampled in August 1975 and four more sites in June 1976, extending to Blossburg, PA, on the Tioga River headwaters.

A number of samples from the 1975 collection were subjected to size fractionation, mineralogical examination, and detailed chemical analysis. The results indicate that for many HM's the ratios of concentration in sand, silt, and clay fractions are relatively constant. These ratios, plus average downstream concentrations and sediment discharge data, provide a basis for calculating the transport of various HM's into Pennsylvania each year from the Susquehanna Basin in New York State. Furthermore, studies of the degree of element-element correlations in the analytical data, and of the uptake and release of Cd(II) and Pb(II) by sediment materials, provide new insights into the mechanism of heavy metal transport in rivers.

Explanatory Note. In this report the following operational size-fraction definitions are assumed unless otherwise noted:

Fraction	Sieve Diameter
sand	2.0 - 0.25 mm
silt	0.25 - 0.004 mm
clay	$\leqslant$0.004 mm

These unusual definitions for sand and silt stem from the fact that an erroneously-labeled U. S. Standard sieve was used to separate sand and silt fractions before chemical analysis (Section II.A.2.c.).

In some cases, a true 0.062 mm sieve was used to separate sand from silt and determine the correct percentages (Section II.A.2.b.), and for such cases the footnote "USGS basis" is added to the text.

All significant discrepancies resulting from these different size-fractionation bases have been corrected in the text.

II. EXPERIMENTAL METHODS

A. SEDIMENT COLLECTION AND FRACTIONATION

1. Selection and Location of Sampling Sites

A series of 22 samples were collected downstream from Binghamton in July 1975 to investigate the relatively high concentrations of Cd, Cr, and Hg (and later, Ag) found in 1974 samples. (See Table I and Figure 1.) This series spanned a total distance of 31 river miles from Johnson City to Barton, N.Y. Two of the sites (#8 and #18) were at 1974 sampling locations. The samples were collected using a twelve foot boat powered by an 8 h.p. motor. A total of twelve samples were taken along the first 15 miles on 7/9/75 and 10 more samples were collected on 7/11/75 in the remaining 16 miles between Owego, N.Y. and Barton. In order to obtain samples that would be reasonably representative, no samples were taken immediately downstream from the point where a tributary or industrial discharge entered the river. As a consequence, the distances between sites varied somewhat.

Samples were also collected in November 1975 after Tropical Storm Eloise to determine if any change occurred in the HM concentration of the sediments as a result of the high flow conditions. In this collection, sites #4, 8, 14 and 18 were resampled, along with the two upstream sites (CK and CB) sampled in 1974.

Two collections were made in the Tioga River sub-basin seeking the source of high Ni and Zn observed at Gang Mills in 1974. In August 1975, the Gang Mills site was resampled and four additional

Table I. Sediment Sampling Sites Downstream from Binghamton Area

Site No.	North Latitude	West Longitude	River Miles*	Location Notes
1	42°06'28"	75°59'40"	1.3	Near Industrial Ponds.
2	42°06'03"	76°01'04"	2.5	0.50 miles upstream from the Rt. 17 Bridge which connects the towns of Vestal and Union.
3	42°05'50"	76°02'00"	3.4	0.40 miles downstream of the Rt. 17 Bridge which connects the towns of Vestal and Union.
4	42°05'37"	76°02'38"	4.1	Adjacent to Union Endicott High School 100 yds downstream from the T.J. Watson Bridge which connects Rt. 17 to Rt. 17C.
5	42°05'24"	76°03'30"	4.9	0.25 miles upstream of the confluence of the Susq. R. and Choconut Creek.
6	42°05'00"	76°05'04"	6.3	0.13 miles upstream from the confluence with Nanticoke Creek; adjacent to the En-joie Golf Course.
7	42°04'44"	76°06'15"	8.3	0.5 miles below the Tri-Cities Airport.
8 (AP)	42°04'30"	76°08'10"	9.2	0.13 miles upstream from Apalachin Sewage Treatment Plant.
9	42°04'57"	76°09'35"	11.2	1.87 miles below the Apalachin Sewage Treatment Plant.
10	42°05'55"	76°10'10"	12.7	2.0 miles above Hiawatha Island.

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*distance downstream from C.F. Johnson Bridge on NY Rt. 201.

Table I (Cont'd)

Site No.	North Latitude	West Longitude	River Miles*	Location Notes
11	42°05'19"	76°11'50"	14.5	0.25 miles above Hiawatha Island
12	42°05'28"	76°13'40"	15.5	200 yds above Bridge which connects Rt. 17 to Rt. 17C below Hickory Park, Owego,NY.
13	42°06'07"	76°15'26"	17.2	0.2 miles upstream from bridge in Owego, NY.
14	42°05'15"	76°16'53"	18.7	0.25 miles downstream from Squaw Island and 0.75 miles downstream of confluence with Owego Creek.
15	42°04'57"	76°18'55"	20.8	0.2 miles downstream of Tuffs Island
16	42°04'03"	76°20'05"	22.3	0.75 miles above the village of Lounsberry, NY; 100 yds upstream from the confluence of Hunts Creek.
17	42°03'12"	76°21'10"	24.7	1.0 miles upstream from confluence with Wappasening Creek.
18 (SB)	42°01'40"	76°22'40"	26.7	0.4 miles upstream from bridge which connects NY Rt. 17 and Rt. 17C below Nichols, NY.
19	42°01'50"	76°23'18"	27.8	0.75 miles downstream from Rt. 282 Bridge in Nichols, NY and 0.25 miles below Hoopers Valley, NY.
20	42°02'00"	76°24'48"	28.9	2.0 miles upstream from Barton, NY.
21	42°02'21"	76°25'51"	29.8	1.1 miles upstream from Barton, NY.
22	42°02'10"	76°28'05"	31.3	0.4 miles downstream from Barton, NY.

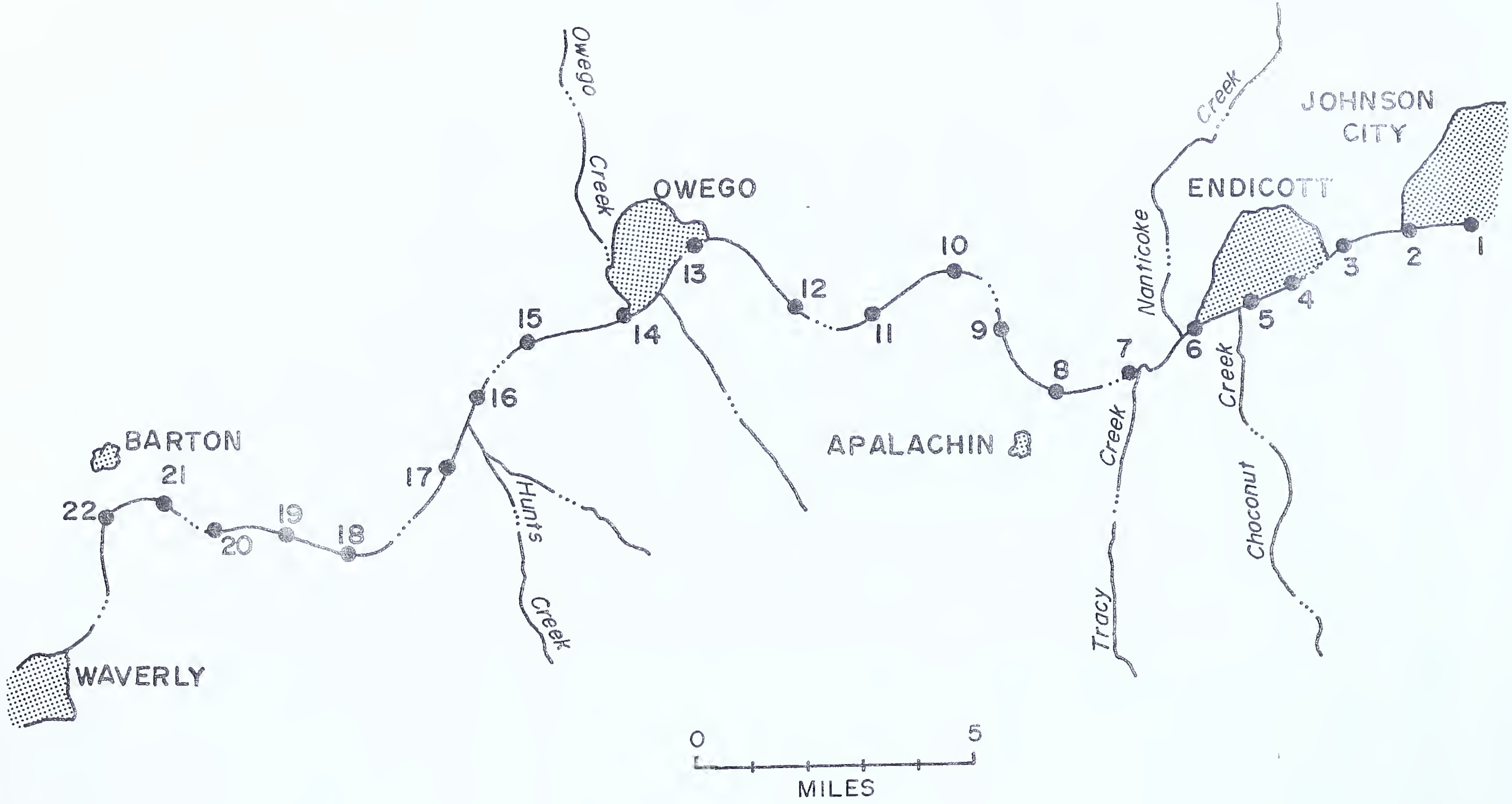

Figure 1. Sites for intensive sampling of Susquehanna River sediment downstream from Binghamton.

upstream sites (A through D) were tested. Then in June 1976 four more upstream sites (E through H) were examined, extending to the Tioga River headwaters at Blossburg, PA, in a coal mining area responsible for considerable acid mine drainage into the Tioga River. These sites are tabulated and shown in Table II and Figure 2, respectively.

2. Methods for Collecting and Fractionating Sediment Samples

a. Standard Sample Collection Procedure

At each sampling site samples were collected from an anchored boat in at least five locations across the river channel within 100 yds upstream or downstream from the starting point. After anchoring the boat at a chosen location, the sample device [a wooden-handle plastic scoop (1)] was scraped along the bottom to collect portions of sample. Each portion was poured into a polyester sieve with 2 mm openings (Dynalab No. 4230) which was over a 5 gallon plastic bucket. The water and sediment material <2 mm passed through the sieve into the bucket and was saved while sediment and debris >2 mm was discarded from the sieve. The process of scooping and sieving at various locations was continued until an estimated 1 kg of sediment material was collected at each sampling site, then the bucket of <2 mm sediment material and water was covered.

Each whole sediment sample in its 5-gal bucket was brought back to the laboratory and allowed to stand overnight. The water was then siphoned off leaving the sand, silt, and clay mixture at the bottom of the bucket. The entire wet unfractionated sediment sample

Table II. Tioga Sub-Basin Sampling Sites, 1974-76

Site Designation	Date and Samples Taken	Location
GM	8/11 & 9/27/74 - Bot. Sed. 8/8/75 - Bot. Sed.	Tioga R., 25-75 yds upstream from gaging station at Mulholland Rd. bridge, 1-1/2 mi. upstream from Gang Mills, NY.
A	8/8/75 - Bot. Sed.	Tioga R., 1 mi downstream from Presho, NY.
B	8/8/75 - Bot. Sed.	Canisteo R., 2 mi upstream from confluence with Tioga R.
C	8/8/75 - Bot. Sed.	Tuscarora Ck., 2-1/4 mi upstream from confluence with Canisteo R.
D	8/8/75 - Bot. Sed.	Canisteo R., 2 mi upstream from Addison, NY.
E (Lindley)	6/17/76 - Bot. Sed. and River Water	Tioga R., 100 yds upstream from bridge at Lindley, NY.
F (Tioga)	6/17/76 - Bot. Sed. and River Water	Tioga R., near first bridge 1/2 mi upstream from Tioga, PA.
G (Crooked Ck)	6/17/76 - Bot. Sed. and River Water	Crooked Ck., near first bridge 1 mi upstream from Tioga, PA.
H (Blossburg)	6/17/76 - Bot. Sed. and River Water	Tioga R., 1/2 mi downstream from Blossburg, PA town line.

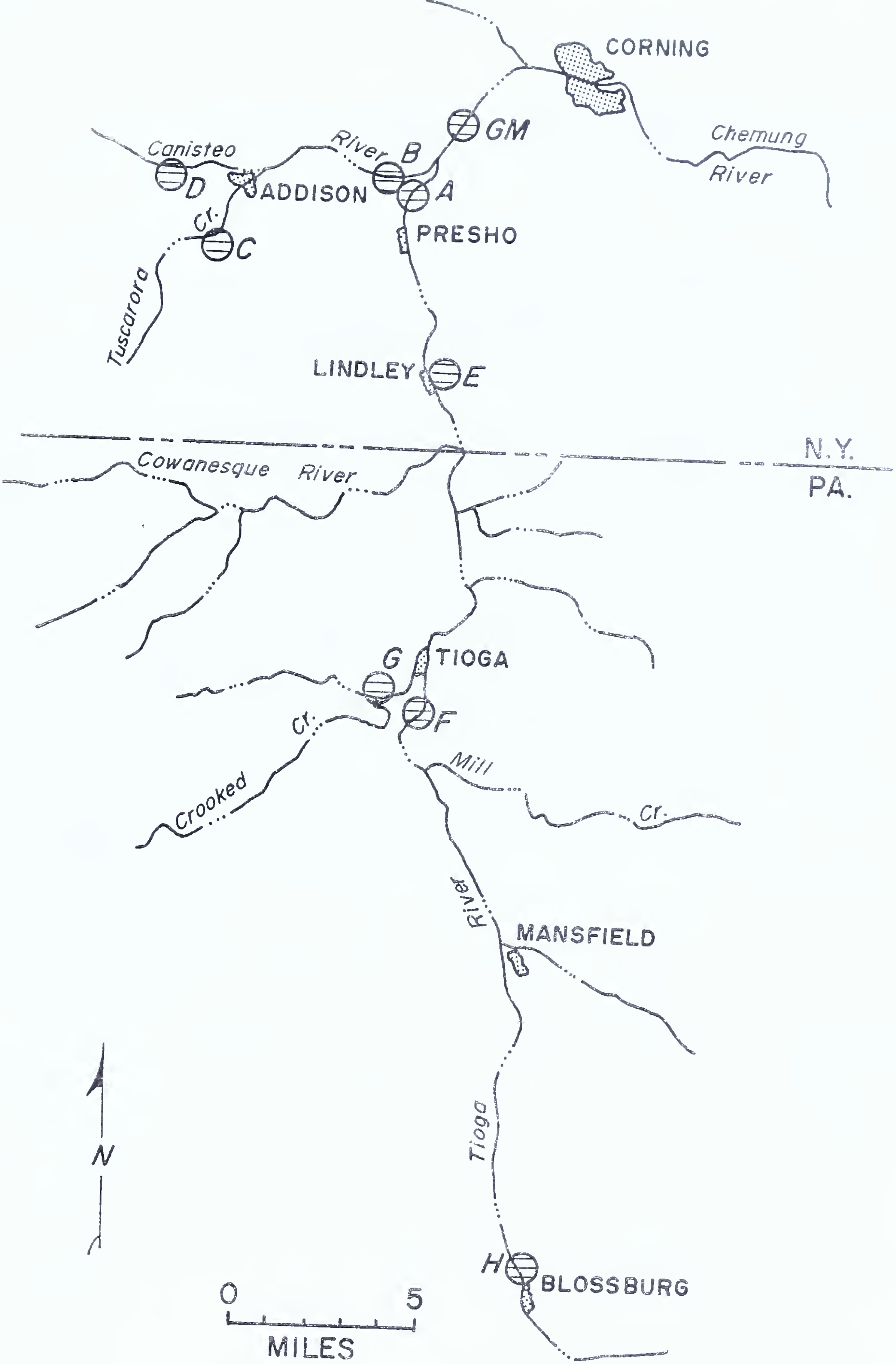

Figure 2. Sampling sites in Tioga River sub-basin, 1974-76.

was then mixed, placed in a quart freezer box, and frozen until fractionation or analysis. The % moisture was determined on separate unfrozen or thawed portions.

b. Determining Percentages of Sand, Silt, and Clay

A 1-3 g portion of air-dried whole sediment sample was wet sieved using a filtering pan with a Tyler Series 250-mesh stainless steel screen (Cistron Corp., Elmsford, N.Y.). The sieving was done using Susquehanna River water collected from Watson Bridge in Endicott, N.Y. near site #4, to simulate natural conditions such as electrolyte concentration, organic content, and heavy metals in the water. The 2.0 to 0.062-mm material* which did not pass through the sieve was collected, oven dried at 105°C, and weighed as per cent sand. The silt-clay slurry which passed through the sieve was collected in a beaker, transferred to a 500 ml graduated cylinder with successive portions of river water (RW), and diluted with RW to a total volume of 500 ml. The suspension was then mixed to achieve a homogeneous suspension.

Based on sedimentation data for 25°C (2), after 38 seconds had elapsed, 25 ml of suspension was withdrawn at a distance of 15 cm below the meniscus, to collect silt and clay, with a settling diameter less than 0.062 mm. The silt-clay mixture remaining in the cylinder was resuspended and after 54 minutes and 25 seconds, a 25-ml portion of the suspension was withdrawn 5 cm down from the meniscus, to collect clay of <.004 mm diameter. The per cent silt was calculated by the following equation after the weight of clay in the 25-ml portion had been subtracted from the silt-clay weight:

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*or 2.0-0.25 mm material, depending on sieve used.

$$\left(\frac{\text{corrected wt of silt}}{\text{total wt of sample}}\right)\left(\frac{500}{25}\right)(100) = \%\ \text{silt} \quad .$$

The % clay was found by the following equation:

$$\left(\frac{\text{wt of clay}}{\text{total wt of sample}}\right)\left(\frac{475}{25}\right)(100) = \%\ \text{clay} \quad .$$

c. Separating Samples into Sand, Silt, and Clay Fractions

The sediment samples were size fractionated after the USGS procedure described by Guy (2). In most cases, the entire mixed <2 mm sediment sample was first wet sieved with river water using a US Series 230 mesh stainless steel sieve. The sand fraction not passing through the sieve (2.0-0.25* mm) was collected, washed with RW to remove any excess clay or silt, and stored in a freezer. The silt-clay slurry which passed through the sieve, containing all the water used to sieve the sand, was saved for further fractionation.

Ideally, a concentration of ∿1 g/ℓ of sediment material should be used when doing a fractionation following Stoke's Law (3). However, because of the time and practicality of collecting an experimentally useable quantity of silt and clay, four-gram portions were used. This amount of the silt-clay mixture was placed in a 1 liter 9-cm diameter jar with 900 ml of river water. The silt-clay suspension was then mixed until a homogeneous mixture was obtained. The temperature of the suspension was recorded and the solutions were allowed to stand for the appropriate time before siphoning off the top 5 cm of clay suspension (2). Each time a withdrawal was made, the clay-water suspension was put into a 250-ml centrifuge bottle and centrifuged immediately on a Sorval RC2-B Super Speed Centrifuge at 5,000 R.P.M. for 5 minutes. After centrifuging, the liquid was decanted back into the original sedimentation flasks so that the silt-clay separation was done in the same volume and same water each time. This was done to limit the amount of "fresh" liquid which would be added to the silt-clay samples, thereby minimizing the leaching of metals from the sediment material.

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*see Explanatory Note, p. 2.

The clay withdrawal procedure was done 5 times on each 4-gram portion of silt-clay mixture, the clay fraction being continuously accumulated in the centrifuge bottle. After the 5th clay withdrawal, the suspension remaining in the 1-liter jar was discarded and the silt was collected from the bottom of the sedimentation flask. This procedure was followed with successive 4-gram portions until the entire silt-clay mixture had been fractionated. The silt fractions were then frozen, and the clay was air-dried and stored.

Test of Purity of the Silt and Clay Fractions. A check of the quality of each collected silt and clay fraction was done on a small representative sample, using the method described above for determining per cent silt and clay, except that 100-ml graduated cylinders and 10-ml portions of the suspension were used for clay fractions, with a 0.1 g sample. It was found that the silt fractions averaged 3% clay and the clay fractions averaged 98% clay.

B. CHARACTERIZATION OF SIZE FRACTIONS

1. Mineralogical Examination

a. Analysis of Sand Fractions by Standard Thin Section Procedure[*]

Sand fractions[*] from the July 1975 and November 1975 samples were impregnated in epoxy glue for preparation of 24 x 40 mm thin section slides. The samples were sliced to 0.06 mm and these thin sections were analyzed in plain polarized light and also under crossed Nicol light using standard petrographic techniques for both the slicing procedure and the polarized light analysis (4). Incident light microscopy was also employed as a technique for identifying the opaque materials present in the sample. The per cent compositions were based on identifications at more than 500 points covering each thin section slide, using a 1.6 mm x 0.2 mm grid to locate the points.

b. X-Ray Diffraction Analysis of Clay Fractions

(1) Mounting of Clay Samples. A weighed 1-2 g representative portion of a standard clay mineral or a clay sample was K^+-saturated by soaking five times in a 1 M KCl solution. The sample was then washed several times with double distilled water (DDW) to free the clay of excess KCl. The K^+-saturated samples were diluted with DDW until a 1-ml portion of the suspension contained 80 mg of sample and then de-aggregated with an ultrasonic vibrator (Bronwill Scientific Div. Biosonik II No. 810 High Intensity Ultrasonic Probe) for 2 minutes. One ml of the sample was placed on a horizontal 25 x 75 mm microscope

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[*] Done by N. Podoff and R. D. Tyler of the SUNY-Binghamton Department of Geological Sciences.

[**] USGS basis

slide and dried at room temperature to maximize parallel orientation of the clay mineral crystals.

(2) X-Ray Diffraction Procedure. The mineralogy of the clay samples was determined by X-ray diffraction using standard procedures (5-9). The clay mounted on a microscope slide was placed on the stationary holder of a General Electric SPG Spectrogoniometer and exposed to a scanning (1°/min) CuK_α radiation source. The X-ray beam passed through a nickel filter prior to reaching the sample to block out CuK_{β_1} radiation. The diffracted beam was detected on a General Electric SPG-8 Counter Tube and recorded on a General Electric XRD-6 X-ray diffraction recorder. The goniometer and recorder were standardized by using a permaquartz specimen (Catalog No. A4954LE) of novaculite which was supplied by the General Electric Company. Large angle (10°-34° 2θ) diffractograms were run using a medium-resolving collimator, 0.2° detector slit, 3° medium-resolution beam splitter, 1000 counts per second attenuation, and a time constant setting of 2.0. High resolution for small angle diffractograms (2°-10° 2θ) was achieved using 1° medium-resolving beam splitter, 0.02° detector slit, medium-resolving collimator, 1000-2000 counts per second attenuation, and a time constant setting of 2.0.

(3) Identification of the Clay Minerals. The diffractograms of clay fractions from the July 1975 samples were compared to those run on API Kaolin #7, API Illite #36, bentonite, and chlorite-illite standards obtained from the SUNY Binghamton Department of Geological Sciences. The bentonite (montmorillonite) standard was a fractionated

<2 μm sample from Glasgow, Montana. The chlorite-illite mixture was fractionated <2 μm sample isolated from the Chenango River, which proved to contain more illite than chlorite. An additional chlorite mineral sample from California (Wards No. 48W) was also run and compared to the unknown clay samples.

The clay mounts from the river sediment material were characterized by exposing them along with the standard clay mounts to systematic physical and chemical treatment and noting changes in the diffraction patterns. The treatments were:

(1) Exposing the samples to 6 M HCl at 60°C for 24 hr, to destroy chlorite diffraction peaks.

(2) (a) Exposing to glycerol at 60°C for 1 hr, to detect the presence of expanding clays, then heating at 300°C after glycolation, to observe peak collapse (characteristic of montmorillonite);

(b) Heating at 500°C in a muffle furnace, to destroy kaolin structure;

(c) Heating at 560°C to eliminate the 2nd- and 3rd-order peaks of chlorite while increasing the intensity of the 1st-order chlorite peak.

2. Determination of Cation Exchange Capacity of Sediment Fractions: K^+-Ba^{2+}

The procedure for determining the CEC of sediment fractions was taken from one developed by Malcolm and Kennedy (10). The weights of sand, silt, and clay taken were 0.5, 0.2, and 0.1 g, respectively. Each sample was placed in a 50-ml Erlenmeyer flask containing 40 ml of a 1 M KCl solution. The solid-liquid suspensions were agitated on a mechanical shaker for 24-48 hours, then the liquid was separated from the solid by centrifugation and 40 ml of fresh 1 M KCl was added to the flasks. This process was continued for a two week period (at least 10 fresh portions of KCl being used) until the sediment material was thoroughly saturated with K^+ ions. Following K^+-saturation, the sediment fractions were washed with DDW to remove excess chloride ion (until no visible sign of AgCl precipitate appeared when the washings were added to 5 ml of 1 M $AgNO_3$ in 0.01 M HNO_3) and air dried.

The dried sediment fractions were mixed on a watch glass and duplicate portions from each fraction were weighed out and placed in 50 ml of 0.2 N $BaCl_2$ in a stoppered Erlenmeyer flask and continuously agitated for a 2 week period. After equilibration, the solutions were separated as follows: sand was allowed to stand for 5 minutes and the supernatant liquid was poured off; solutions from the silt and clay suspensions were filtered through a 0.45 μm Millipore filter. The concentration of K^+ displaced by Ba^{2+} into the solution was determined by atomic absorption (AA), using the 7664 A line from a K-vapor lamp and standard settings. The absorbance calibration curve prepared from KCl dissolved in 0.2 N $BaCl_2$ was linear up to a K^+ concentration of 5 mg/l.

C. CHEMICAL ANALYSIS OF SEDIMENT SAMPLES AND SIZE FRACTIONS

The procedures for chemical analysis were described in detail in the previous report (1). The method of Malo for determining surficial heavy metals (11), based on a 10-min treatment of the samples with 30% H_2O_2 followed by addition of 0.3 M HCl and digestion at near-boiling for 30-45 min, was again used. All samples or size fractions were analyzed in duplicate.

Portions of the final "surficial" solution were analyzed by AA for the heavy metals Ag, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn, and by special AA procedures for As (following AsH_3 generation) and for Hg (the cold vapor technique). In the Hg procedure, to determine "surficial" Hg instead of "total" Hg as in the previous work (1), 30-50 ml of the surficial solution were diluted to 100 ml with 10% H_2SO_4 (to minimize foaming), then $KMnO_4$ was added to a persistent color, N_2 was bubbled through the solution to establish the instrument "zero" line, and 10 ml of the hydroxylamine-$SnCl_2$ solution were added to generate the Hg^o peak as in the usual Hatch and Ott procedure (12).

Total organic carbon was determined as before by the chemical oxygen demand procedure of Jackson (13).

D. UPTAKE AND RELEASE OF Cd(II) AND Pb(II) BY SEDIMENT MATERIALS*

Four materials were used in this study: illite (API #36), California chlorite (Ward's # 48W), an illite-chlorite mixture from the Chenango River (SUNY-Binghamton Dept. of Geol. Sci.), and natural suspended solids (NSS) low in Cd and Pb (the silt/clay fraction of a 1974 bottom sediment sample from Gang Mills, N.Y., on the Tioga River).

The uptake of Cd(II) and Pb(II) were measured separately in a synthetic RW medium of pH 7.50, prepared with the following millimolar concentrations: Na^+ 0.34, K^+ 0.035, Ca^{2+} 0.85, Mg^{2+} 0.20, NH_4^+ 0.017, NO_3^- 0.008, $H_2PO_4^-/HPO_4^=$ 0.0030, $H_2CO_3/HCO_3^-/CO_3^=$ 1.7,

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*Taken from the doctoral dissertation of I. El-Barbary (14).

SO_4^{-2} 0.20, Cl^- 0.38. Concentrations of Cd(II) and Pb(II) ranging from 1-3 μg/ℓ to 3-10 mg/ℓ were equilibrated at 25°C in 50-ml Erlenmeyer flasks with the sediment materials in the proportion: 50 ml of spiked synthetic RW to 25 mg of sediment material. After equilibration, the solutions were separated by centrifugation and analyzed for total soluble Cd or Pb using the method of differential-pulse anodic stripping voltammetry. Blanks were run to correct for adsorption on the walls of the flasks.

Release of Cd(II) or Pb(II) was measured from loaded sediment materials into the following media: (1) synthetic RW @ pH 7.5; (2) synthetic RW adjusted to pH 3.0, using HCl for Cd(II) or HNO_3 for Pb(II); (3) synthetic RW plus 1 mg/ℓ of Na_2EDTA, @ pH 7.1; (4) synthetic sea water, at pH 7.7; (5) 1.0 N strong electrolyte: $MgCl_2$ for Cd(II), $Mg(NO_3)_2$ for Pb(II). The proportions 25 mg of loaded sediment material to 50 ml of release medium were used. After a 48-hr equilibration period, the solutions were separated and analyzed as above or by AA.

III. RESULTS AND DISCUSSION

The results of chemical analyses of sediment samples are presented in Tables III, IV, and V. Each chemical result is the average of duplicate determinations. In Table III, analyses for % C and seven surficial metals in whole, unfractionated samples from the 22 downstream sites are given, along with the percentages of sand, silt, and clay in the samples. In Table IV, results on analysis of % C and 11 metals in the sand, silt, and clay fractions of four samples taken in July 1975 [Sites #4, 8 (AP), 14, and 18 (SB)] and six samples in November 1975 [same four sites, plus CK and CB] are shown, along with the results of CEC determinations. Table V presents analytical results on sediment and water samples collected in 1975 and 1976 from sites in the Tioga River sub-basin of the Chemung basin.

A comparison of the precision of 1974 and 1975 sediment analyses is given in Table VI, as relative standard deviations calculated from pooled duplicate determinations. The average precisions for 1975 sand, silt, and clay analyses were 10%, 9% and 13%, respectively, compared to an average of 17% for 1974 samples (1). Improvements in precision were noted for the elements As, Cd, and Pb, which may reflect improved laboratory techniques in the second year of the sediment study. (Increased sample homogeneity, if a significant factor, would have improved the precision for all elements, not just the three cited.)

Table III. Results of July 1975 Sediment Sampling Downstream from

Johnson City Bridge (Rt. 201) to Pennsylvania Stateline

Site #	Distance Downstream, River Miles	Size Distribution* %Sa	%Si	%Cl	Organic Carbon %	Surficial Metals, µg/g Ag	As	Cd	Cr	Cu	Mn	Hg
1	1.3	91.3	8.3	0.4	0.76	13.0	0.21	6.0	5	10	248	0.055
2	2.5	88.7	10.9	0.4	1.19	6.8	0.23	3.2	7	14	216	0.094
3	3.4	83.8	15.8	0.4	0.94	8.2	0.21	4.6	7	17	305	0.054
4	4.1	89.4	10.0	0.6	0.97	19.9	0.19	14.4	10	31	267	0.057
5	4.9	92.5	7.1	0.4	0.55	7.3	0.20	7.6	6	13	355	0.065
6	6.3	68.5	31.0	1.5	1.89	14.4	0.24	6.7	8	26	218	0.158
7	8.3	93.9	5.8	0.3	0.53	3.6	0.20	3.5	6	13	190	0.136
8	9.2	79.6	19.5	0.9	1.32	9.1	0.23	7.1	12	22	209	0.137
9	11.2	82.1	16.9	1.0	1.32	7.3	0.23	3.3	6	34	300	0.182
10	12.7	91.2	8.2	0.6	0.72	5.7	0.22	3.4	9	15	335	0.107
11	14.5	69.8	28.4	1.8	1.67	9.1	0.27	5.1	8	23	201	0.103
12	15.5	76.0	23.0	1.0	1.74	13.6	0.47	6.0	20	22	257	0.177
13	17.2	94.0	5.5	0.5	0.29	2.6	0.25	2.5	5	14	394	0.068
14	18.7	94.6	5.0	0.4	0.45	2.1	0.21	2.3	4	14	401	0.058
15	20.8	71.3	27.7	1.0	1.98	13.4	0.56	8.1	14	28	420	0.126
16	22.3	72.8	26.4	0.8	1.73	6.3	0.45	4.2	9	22	238	0.039
17	24.7	72.9	27.0	0.1	1.80	8.0	0.58	5.6	11	29	329	0.048
18	26.7	70.2	27.3	2.5	1.76	11.0	0.34	8.9	8	27	406	0.069
19	27.8	81.2	17.0	1.8	1.03	4.4	0.45	3.9	7	17	226	0.016
20	28.9	86.0	13.7	0.3	1.49	5.9	0.47	4.3	13	19	220	0.032
21	29.8	70.0	28.5	1.5	1.46	8.4	0.57	5.0	13	19	357	0.036
22	31.3	91.1	7.8	1.1	1.10	4.0	0.50	2.6	23	12	363	0.014
Av.		82.3	16.8	0.9	1.15	8.8	0.33	5.4	10	24	293	0.083
Range		68- 95	5- 31	0.1- 2.5	0.5- 1.98	2.1- 14.4	0.19- 0.58	2.3- 14.4	4- 23	9- 33	216- 420	0.014- 0.182

*USGS basis(see Note, p. 2)

Table IV. Analysis of 1975 Sediment Fractions from Susquehanna Sub-Basin Sites

Sampling Date	Fraction Analyzed	% of Sample	Surficial Concentrations, µg/g (dry wt)											Total Org. Carbon, %	CEC meq/100 g
			Ag	As	Cd	Cr	Cu	Fe (mg/g)	Hg	Mn	Ni	Pb	Zn		
Site #4	%	*													
7/11/75	Sand, 67.8	89.4	6.0	0.17	6	7	25	8.9	.072	252	22	43	86	0.35	4.0
	Silt, 31.6	10.0	31.0	0.28	22	13	64	6.8	.169	385	29	52	126	1.68	6.0
	Clay 0.6	0.6	196.	2.05	58	51	388	10.1	.85	301	158	149	501	3.83	--
	Total (calc)		15.1	0.21	11	9	39	8.2	.107	295	25	46	101	0.79	~4.6
11/24/75	Sand, 92.0	93.4	3.8	0.21	3	85	222	6.3	.394	289	14	145	156	6.2	4.2
	Silt, 7.4	6.0	9.7	0.29	4	62	31	10.0	.102	556	21	37	81	1.88	5.8
	Clay, 0.6	0.6	11.0	2.45	6	18	92	29.0	.401	1294	58	<100	148	2.50	16.5
	Total (calc)		4.3	0.22	3	83	207	6.7	.315	315	15	136	151	5.8	4.4
Site #8 (Apalachin)		*													
7/11/75	Sand, 66.4	79.6	3	0.20	3	10	19	9.8	.107	244	18	15	82	0.27	3.8
	Silt, 32.7	19.5	13	0.30	11	13	64	8.3	.140	304	25	37	103	2.03	--
	Clay, 0.9	0.9	69	2.25	31	43	362	12.6	1.33	198	112	81	389	3.73	--
	Total (calc)		7	0.25	6	11	37	9.3	.129	263	21	23	92	0.87	~4.2 (est.)
11/24/75	Sand, 85.5	89.0	4	0.24	~1	2	9	4.2	.026	257	8	15	42	0.58	3.1
	Silt, 13.7	10.2	12	0.34	7	13	35	10.5	.132	501	20	32	95	1.85	4.9
	Clay, 0.8	0.8	21	3.08	<5	30	108	35.0	.381	396	54	<100	146	2.52	10.0
	Total (calc)		5	0.27	2	4	13	5.3	.043	292	10	17	50	0.77	3.[illegible]

*USGS basis (see Note, p. 2)

Table IV. (Cont'd)

Sampling Date	Fraction Analyzed	% of Sample	Surficial Concentrations, µg/g (dry wt)											Total Org. Carbon, %	CEC meq/100 g
			Ag	As	Cd	Cr	Cu	Fe (mg/g)	Hg	Mn	Ni	Pb	Zn		
Site #14	%	*													
7/11/75	Sand, 87.7	94.6	<2	0.25	<1	5	14	10.1	.039	408	15	27	62	0.20	4.8
	Silt, 11.9	5.0	9	0.37	9	8	99	7.3	.167	1174	23	62	102	1.88	6.6
	Clay, 0.4	0.4	86	4.27	20	33	585	6.4	.80	453	160	125	477	4.32	--
	Total (calc)		3	0.28	2	6	26	9.7	.057	500	17	32	68	0.42	~5.0
11/24/75	Sand, 77.9	93.5	2	0.21	0.7	7	17	6.0	.098	337	10	21	40	0.87	4.5
	Silt, 21.6	6.0	3	0.51	1.0	7	14	6.5	.075	208	13	19	46	1.24	3.5
	Clay, 0.5	0.5	30	2.91	<4.1	41	112	35.1	.586	1773	60	<100	185	4.02	16.2
	Total (calc)		2	0.28	0.8	7	17	6.2	.085	317	11	21	42	0.97	4.4
Site #18 (Smithboro)		*													
7/12/75	Sand, 61.0	70.2	<2.4	0.27	1.2	4	20	7.3	.038	238	11	16	63	0.34	4.0
	Silt, 36.5	27.3	11.0	0.40	7.5	13	82	9.5	.206	511	27	34	104	2.30	7.3
	Clay, 2.5	2.5	37.0	2.37	4.8	25	341	11.4	.496	257	98	85	296	3.54	--
	Total (calc)		6.4	0.37	3.6	8	51	8.2	.110	338	19	24	84	1.14	~5.1
11/24/75	Sand, 77.6	84.9	1.0	0.24	0.7	6	10	6.8	.027	280	12	16	37	0.62	3.2
	Silt, 22.3	15.0	4.0	0.40	2.6	9	24	8.2	.120	511	17	26	58	1.54	4.6
	Clay, 1.0	1.0	8.0	2.58	4.8	32	81	29.4	.486	1540	61	<100	159	3.04	16.2
	Total (calc)		1.8	0.30	1.2	7	14	7.4	.053	346	14	18	43	0.85	3.7

*USGS basis (see Note, p. 2)

Table IV. (Cont'd)

Sampling Date	Fraction Analyzed	% of Sample	Surficial Concentrations, µg/g (dry wt) Ag	As	Cd	Cr	Cu	Fe (mg/g)	Hg	Mn	Ni	Pb	Zn	Total Org. Carbon, %	CEC meq/100 g
Site CK (Conklin)															
11/25/75	Sand, 91.8	94.5*	0.8	0.24	0.5	2	12	3.9	.014	533	8	21	23	0.86	4.7
	Silt, 7.4	4.7	1.5	0.31	0.8	5	26	13.0	.066	580	18	27	68	1.88	6.6
	Clay, 0.8	0.8	<7.6	1.93	<3.8	28	103	30.8	.525	674	64	<100	144	2.76	12.1
	Total (calc)		0.9	0.26	0.6	2	14	4.8	.022	537	9	22	27	0.95	4.9
Site CB (Chenango Bridge)															
11/25/75	Sand, 91.2	95.0*	0.8	0.24	<0.6	4	7	4.8	.013	304	8	50	42	0.98	1.4
	Silt, 8.0	4.2	0.9	0.29	0.5	6	39	11.0	.092	499	25	29	86	2.10	9.4
	Clay, 0.8	0.8	<19.0	3.65	<9.2	29	22	24.0	.466	1054	70	<100	163	4.70	16.1
	Total (calc)		1.0	0.27	0.7	4	10	5.5	.022	325	10	48	46	1.10	2.2

*USGS basis (see Note, p. 2)

Table V. Analysis of Sediment and Water Samples from Tioga Sub-Basin Sites*

Site	Sample		Ag	Cd	Cr	Cu	Ni	Pb	Zn	Fe (mg/g)	Mn	pH	Spec. Cond.
GM: 1974 (Av. of 2)	Sed		--	0.4	4	13	40	--	188				
8/8/75	Sed		--	3.2	1	9	7	--	28				
A	Sed		--	1.7	1	13	26	--	108				
B (Canisteo R)	Sed		--	1.2	1	10	6	--	27				
C (Tuscarora Ck)	Sed		--	<0.5	1	4	4	--	13				
D (Canisteo R)	Sed		--	<0.5	2	8	4	--	22				
		%											
E	Sand	33.6	<0.5	<0.6	--	13	21	<18	118	5.6	376		
	Silt/Clay	66.4	<0.6	<0.7	--	24	33	<22	282	8.0	570		
	Av Sed		<0.6	<0.6		20	29	<21	227	7.2	505		
	River Water		--	--	--	3	24	<30	190	--	--	7.2	354
F	Sand	85.3	<0.5	<0.6	--	11	10	<18	76	5.6	370		
	Silt/Clay	14.7	0.7	<0.7	--	25	20	38	209	5.0	487		
	Av Sed		<0.5	<0.6		13	12	<21	96	5.5	387		
	River Water		--	--	--	4	44	<30	220	--	--	6.6	320
G (Crooked Ck)													
	Sand	59.1	<0.5	<0.6	--	8	9	<19	31	6.5	266		
	Silt/Clay	40.9	<0.6	<0.7	--	8	9	<20	38	7.2	276		
	Av Sed		<0.6	<0.6		8	9	<19	34	6.8	270		
	River Water		--	--	--	2	<14	<30	<2	--	--	7.4	310
H	Sand	75.4	<0.5	<0.7	--	11	5	19	48	5.9	356		
	Silt/Clay	24.6	0.8	0.8	--	36	10	158	486	6.6	561		
	Av Sed		<0.6	<0.7		17	6	53	154	6.1	406		
	River Water		--	--	--	5	42	87	310	--	--	4.3	358

*Sediment concs. in μg/g; river water concs. in μg/ℓ.

Table VI. Precision of Chemical Analyses

Element	Rel. Std. Dev., %* 1974 Samples Whole and Fractional Samples	Rel. Std. Dev., 1975 Samples		
		Sa	Si	C
As	29	6	6	[illegible]
Ag	---	4	11	28
%C	13	13	15	4
Cd	39	13	12	[illegible]
Cr	11	18	8	10
Cu	10	14	6	10
Fe	7	7	7	7
Hg	20	4	7	28
Mn	---	26	6	10
Ni	12	10	13	22
Pb	34	4	8	11
Zn	4	6	4	10
Av.	17	10	9	13

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*From pooled duplicates of 28 samples, except %C which had 5 samples (1).

‡From pooled duplicates on sand, silt, and clay fractions of the 10 samples of Table IV.

A. SPATIAL AND TEMPORAL COMPARISONS OF HM CONCENTRATIONS

In this section, four topics are presented: (1) the July 1975 profiles of HM concentrations in Susquehanna sediments downstream from Binghamton, (2) changes in the HM concentrations of sediments at selected sites in 1975 after the near-flooding of Tropical Storm Eloise, (3) average element concentrations in 1974-75 sediment samples for principal sites, and (4) a search for the sources of high Ni and Zn in Tioga River sediments.

1. HM Concentration Profiles in Sediments Downstream from Binghamton

The average downstream concentrations reported in Table III are comparable to those found in 1974 for Sites #8 (Apalachin) and #18 (Smithboro) (1). The range of values was from ∿0.4X to ∿2X the average for the various elements determined.

Part of the fluctuation in whole sample concentrations can be attributed to large differences in particle size distribution among the samples. For example, the percentages of silt ranged from 5 to 31%. Thus, before plotting the downstream profiles, it seemed advisable to "normalize" the values as follows: using the sand/silt/clay concentration ratios established below for the various elements (see Section III.B.3), and using the size distribution in each sample, the concentrations for the various elements in each sand fraction were calculated (see Appendix A).

The normalized metal concentrations for Ag, Cd, Cu, and Hg in the sand fractions are plotted in Figure 3 versus river miles downstream

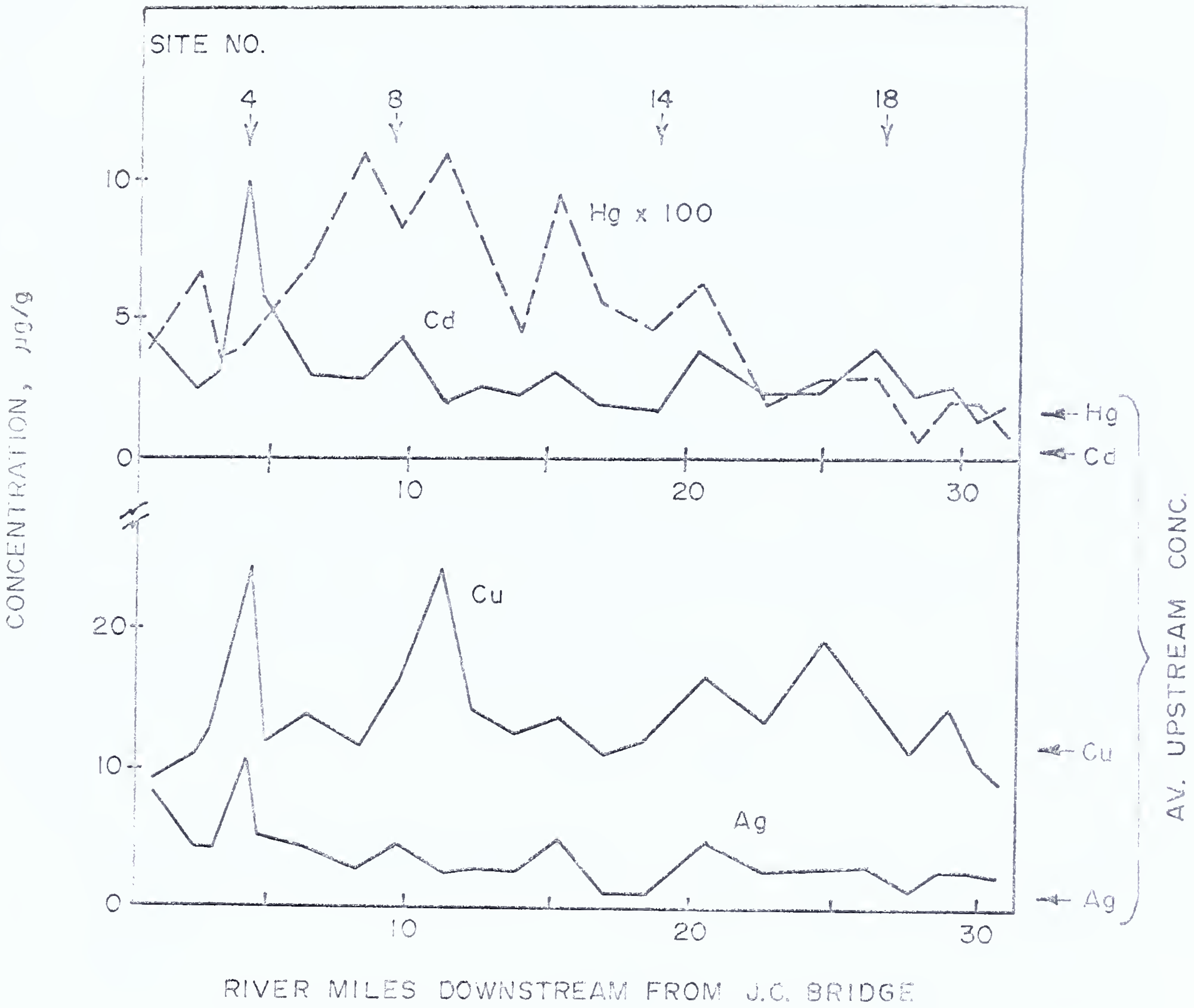

Figure 3. Downstream profile for trace metals in sand fraction of July 1975 bottom sediments.

from the Johnson City bridge. The results show that Ag, Cd, and Hg were indeed higher near Binghamton, decreasing with distance to values approaching the 1974 upstream "baseline" levels. Thus these curves show (1) the impact of this urban area and (2) the degree of persistence of this heavy metal pollution as the sediments move downstream (assuming no additional downstream pollution inputs). The fact that the concentrations tended to decrease downstream could be due to gradual leaching by the river water and to "dilution" by the addition of uncontaminated sediments from downstream tributaries and bank erosion. [The fact that the fluctuations in Ag and Cd correlate so well is surprising, but is probably associated with their simultaneous discharge (until recently) from a GAF photographic film plant in Binghamton which discharged approximately 10-20 kg/day of Ag (and unspecified amounts of Cd) into the Chenango River in Binghamton (15)]. The normalized concentrations of Cu showed erratic elevations above the baseline, while As and Cr seemed to increase in concentration with distance.

2. Sediments Before and After Tropical Storm Eloise

In late September 1975, Tropical Storm Eloise caused flooding in the Susquehanna River sub-basin in New York State, thus in November 1975 additional sediment samples were collected. The impact of this storm on the bottom sediments can be seen in Figure 4, which shows the July '75/Nov. '75 ratio of element concentrations for the sand, silt and clay fractions at four downstream stations (#4, 8, 14, and 18). The graph shows that the July '75 sediments were distinctly higher in Ag (2 to 5X), Cd (5 to 8X) and Cu (2 to 4X) in all three size fractions,

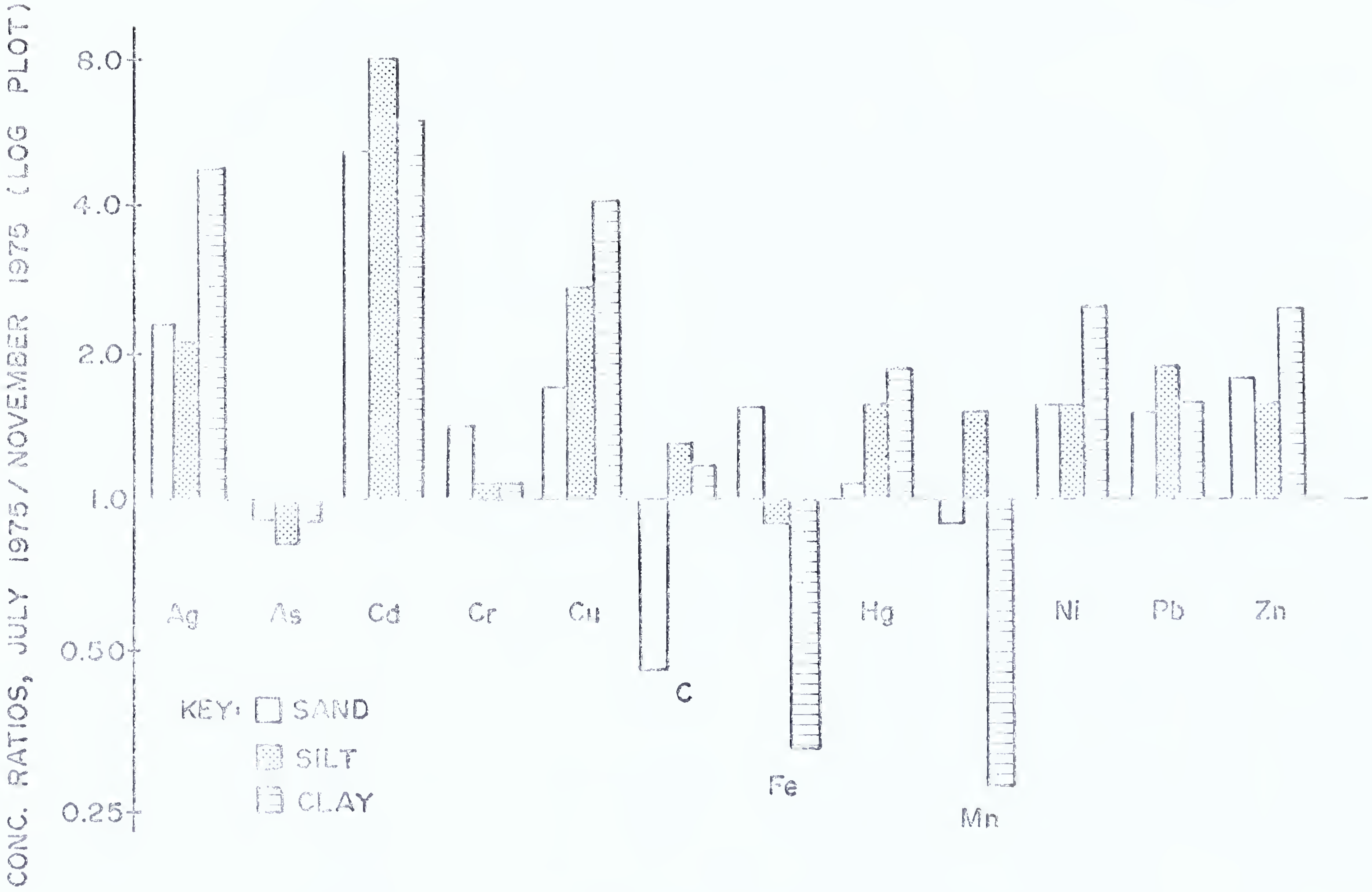

Figure 4. Impact of Tropical Storm Eloise: ratios of concentrations of surficial heavy metals and total organic carbon, before (July 1975) and after (November 1975) the Storm, in sand, silt, and clay fractions.

as compared to post-Eloise samples. Mercury, Ni, Pb, and Zn were somewhat higher in July than in November, but As and Cr showed no significant difference.* There were surprising increases in Fe and Mn in clay fractions and in % organic C in the sand fractions after the storm.

The downstream samples from November 1975, although lower than previous collections in many elements, were nonetheless higher in all elements except % C than the upstream November 1975 samples from sites CK and CB. These upstream samples were about the same after the high flow conditions as in 1974 (1) except for an increase in % C in the sand fraction. This increase in % C in sand after high flow for both upstream and downstream could be related to the type of organic material in the sediments. It is likely that during the high flow, large organic detritus fragments (leaves and twigs) were washed into the river. Further, the increase in % C was not accompanied by an increase in the CEC value, indicating that the organic inputs were at least not rich in humic acid, and probably (like wood or leaf fragments) had a low specific surface area.

3. Average Element Concentrations at Principal Sites, from 1974-75 Sediment Samples

Grand average sediment concentrations for the principal sites in the Susquehanna River Basin in New York State (SRB-NYS) are given in Table VII, based on 1974 data (1) and the data of Table IV. The concentrations range from 0.012 μg/g for Hg to 12.6 mg/g (i.e., 1.26%) for Fe, the order of increasing concentrations generally being

$$Hg \ll As \cong Cd < Ag \cong Cr < Cu \cong Ni \cong Pb < Zn < P \cong Mn \ll C < Fe$$

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*de Groot and Allersma observed that Rhine R. mud was ∿2 x higher in Cu, Cr, Hg, and Zn than flood-plain or "erosion" mud (34).

Table VII. Grand Averages of Sediment Analyses (μg/g unless otherwise noted)

Element	Chemung Sub-Basin (1974)				Upper Susquehanna Sub-Basin (1974 & 1975)				Range	Median	Average
	CP →	(GM) →	BF →	CH	SB ←	AP ←	(CB) ←	CK			
Ag	--	--	--	--	4.	5.	1.0	0.9	0.9-4.	(2.)	(2.7)
As	0.27	0.40	0.32	0.30	0.49	0.24	0.25	0.31	0.24-0.40	0.31	0.32
Cd	0.4	0.4	0.2	0.3	2.1	4.	.5	0.6	0.2-4.0	0.4	1.0
Cr	4.	4.	4.	4.	8.	14.	4.	4.1	4.-14.	4.	6.0
Cu	14.	13.	13.	11.	25.	25.	9.	15.	9.-24.	13.	16.
Fe, mg/g	9.2	9.7	8.6	9.6	10.1	9.8	8.	12.7	8.0-12.6	9.6	9.7
Hg	0.012	0.026	0.017	0.012	0.073	0.098	0.016	0.022	0.012-0.095	0.019	0.034
Mn	--	--	--	--	335.	273.	320.	541.	269.-543.	(328.)	(367.)
Ni	16.	40.*	18.	18.	20.	22.	13.	18.	13.-40.	18.	20.
Pb	9.	7.	37.	14.	20.	23.	26.	22.	7.-37.	21.	20.
Zn	56.	188.*	84.	65.	61.	74.	41.	64.	41.-188.	64.	78.
P	270.	202.	218.	302.	328.	305.	318.	216.	202.-328.	286.	270.
%C	0.65	0.36	0.10	0.23	0.81	1.14	0.50	0.47	0.10-1.03	0.48	0.52

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*The source of high Ni and Zn at the Gang Mills site is discussed in Section III.A.4

In general, sites SB and AP have higher concentrations (except for Fe, Ni, and Zn) than the other sites in the basin. Further comparisons should probably await additional data from the Chemung sub-basin sites, which were not sampled in 1975.

4. Sources of High Ni and Zn in Tioga River Sediments (see Table V)

In the samples of 8/8/75, site A upstream on the Tioga River (Fig. 2) was high in Ni and Zn, while the tributary sites B, C, and D were low in these elements. Surprisingly, the resampling at Gang Mills was low in Ni and Zn, but this anomalous result could be explained if sediment from the Canisteo tributary had washed into the Tioga River prior to sampling, diluting the sediment at Gang Mills.

The additional upstream sampling of water and sediment on 6/17/76 showed that the water at Blossburg (site H) of pH 4.3 was high in Ni and Pb, and very high in Zn, and the sediment was high in Pb and Zn. Moving downstream, at Tioga (site F) and Lindley (site E), Ni increased in the sediments and remained relatively high in water, even though the pH had increased to 6.6 at F and 7.2 at E. Sites F and E were also high in Zn, in both sediments and water, but low in Pb. The tributary site G was low in all metals, in water and in sediment. [Copper was relatively low throughout all these samplings.]

Thus the pattern appears to be one of high Ni, Pb, and Zn in acid mine drainage from the Blossburg area, with hydrolysis and enrichment in the sediments evident at Blossburg for Pb and Zn, and increasingly at Sites F, E, and A for Ni. Further downstream, however, inputs from tributaries may increasingly mask the high Ni and Zn sediments.

It is interesting that Fe was not particularly high in any of these acid mine-drainage sediments.

A detailed examination of the 6/17/76 sand and silt-clay analyses showed a steady increase in Ni in sand and silt-clay fractions from Blossburg through Tioga to Lindley, and a steady increase in Zn in the sand fractions. However, Zn was highest (486) in the silt-clay fraction at Blossburg and lower by about a factor 2 at Tioga and Lindley. This suggests some loss of Zn from the silt-clay fraction to the sand fraction as the silt moves downstream. The Blossburg silt-clay fraction also had a high concentration of Pb (158) which dropped to 38 at Tioga, elevated Cu (36), and detectable concentrations of Ag (0.8) and Cd (0.8).

B. PHYSICAL AND CHEMICAL CHARACTERIZATION OF BOTTOM SEDIMENTS FROM THE SUSQUEHANNA SUB-BASIN IN NEW YORK

1. Mineralogy

a. Particle-Size Distribution

When bottom sediment samples are examined as to size distribution* (Tables III and IV), the striking features are the low percentage of clay (usually <1%), the large percentage of sand, and the variability in percentage of silt (from 5 to 31%). Using size distribution data for the September 1974 samples (reference 1) and the 1975 data, averages for the principal "downstream" sites of the Chemung sub-basin (Big Flats and Chemung) and the Upper Susquehanna sub-basin (Apalachin and Smithboro) were obtained. Then, using the ratio of 1.0 to 1.8 for discharge of sediment from the two sub-basins, respectively (16), the following weighted-average size distribution* was calculated for downstream sediments:

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*USGS basis

sand 76 ± 20%; silt 23 ± 21%; clay 0.8 ± 0.8%

(These percentages are used later with overall analyses and sand/silt/clay concentration ratios to calculate the best average concentrations of HM's in downstream sand, silt and clay fractions.)

b. Sand Fractions

The results of the thin section mineralogical examination of selected sand fractions* are given in Table VIII. The bulk of the sand-size material in all the samples consisted of quartz, rock fragments (sandstone, siltstone, and shale), and feldspars. Sample CB had a considerable amount of quartz (47.0%) which may acount for its low cation exchange capacity. (See Table X). Many of the samples, especially sample 4B, had appreciable amounts of opaque (i.e., black) material which was identified tentatively as either some type of oxide or burned coal "clinker." Also sample 4B was relatively rich in limestone, which was present also in samples 4A and CB, but was otherwise absent. The anomalously high percentages of opaque material and limestone in 4B may account for the higher % C, Cr, Cu, Hg, Pb, and Zn found in that sample (see Table IV).

c. Clay Fractions

Figures 5a-5d show X-ray diffractograms for illite, chlorite, and the clay fraction of sediment from Site #18, with the effect of HCl

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*USGS basis

Table VIII. Percentage Composition of Sand Fractions, from Thin Section Analysis*

	DOWNSTREAM (A samples - July '75; B samples - Nov. '75)								UPSTREAM (Nov. '75)	
Phase	4A	4B	8A	8B	14A	14B	18A	18B	CK	CB
Quartz	31.1	18.0	28.0	28.9	29.7	32.4	29.0	33.6	12.1	47.0
Feldspar	3.9	3.8	2.9	5.4	4.7	5.3	3.0	4.4	1.6	3.4
Opaque†	5.8	17.4	1.7	1.5	0.5	0.2	0.4	0.6	7.6	0.5
Rock Fragments:										
a) Sandstone & coarse siltstone	28.3	27.1	31.7	32.4	39.2	32.4	38.3	33.8	34.5	27.9
b) Siltstone & shale	26.4	15.6	31.7	28.1	24.1	24.5	24.6	17.8	40.7	11.6
c) Limestone	1.5	13.8	--	--	0.2	--	tr	--	--	4.1
d) Metamorphic & igneous	2.2	2.2	2.3	2.8	0.2	4.8	3.9	9.1	1.2	5.2
Other Minerals:										
Garnet	0.7	tr	0.4	--	0.5	0.4	0.6	0.4	tr	tr
Pyroxene	tr	tr	--	0.4	tr	tr	0.4	tr	--	0.2
Zircon/Sphene	-/tr	--	tr/-	0.4/tr	--	--	--	--	--	--
Epidote	--	--	tr	--	tr	tr	--	--	--	--
Amphibole	--	tr	0.6	--	tr	--	tr	tr	1.2	--
Glass	--	2.2	--	--	--	--	--	0.2	--	--
Unknowns (red-brn. fibrous material)	--	--	0.4	0.4	--	--	--	--	0.2	--

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[*] Based on 500+ point counts, using a 1.6 x 0.2 mm grid and standard petrographic identification techniques (by Ronald D. Tyler).

[†] Oxide or burned coal (i.e., "clinkers"); some burned coal is definitely present.

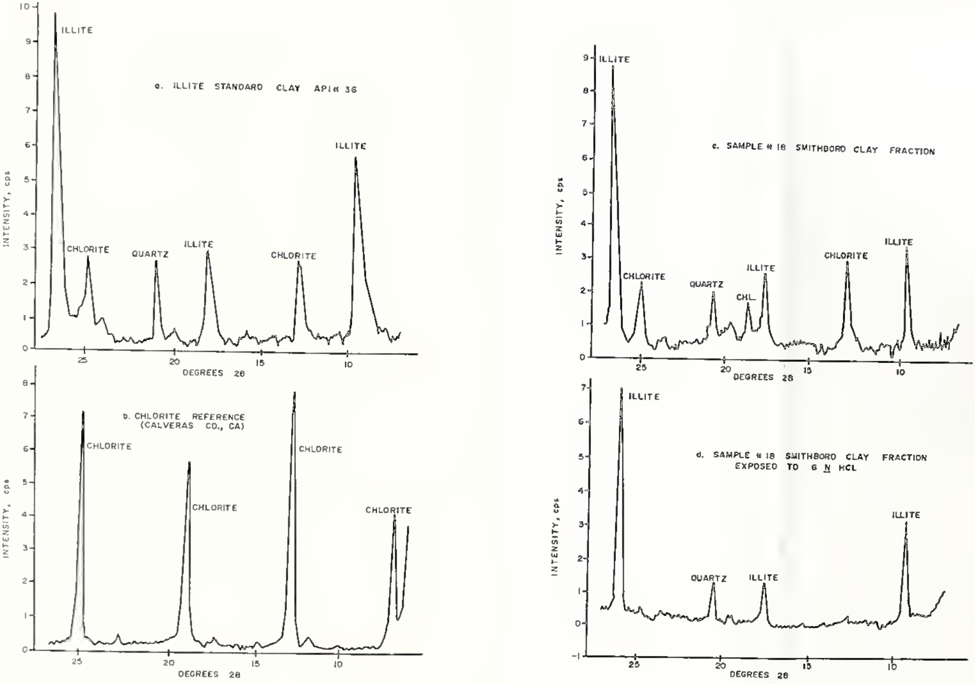

Figure 5. X-ray diffractograms of clay materials.

treatment. Table IX summarizes the findings for reference clays and clay from Sites 4, 8, 14, and 18. From these results it is evident that clay fractions from the July 1975 samples are a mixture of illite and chlorite, or an illite-chlorite interlayered clay mixture. Similar X-ray results were obtained on clay fractions from the November 1975 samples. From diffractograms on known varying concentration mixtures of chlorite and illite, compared to the diffractograms of unknowns, it was determined that the clay samples contained illite and chlorite in approximately a 6/4 ratio. In the figures, the peaks at 6.3°-2θ, 12.6°-2θ, and 25°-2θ correspond, respectively, to the interplanar d-spacings 14A, 7A, and 3.5A of chlorite, while the 8.9°-2θ and 17.8°-2θ peaks represent, respectively, the 10A and 5A d-spacings of illite. The diffractograms also showed that neither montmorillonite nor kaolinite were present to a significant extent in these clay samples from the Upper Susquehanna sub-basin sediments. From the 6 N HCl treatment, which would eliminate any chlorite mineral, the chlorite peaks present in all the unknown fractions were lost in every case. Further identification of the chlorite mineral was obtained when the 14A (001) d-reflection increased in intensity after heating to 560°C while the remaining d-reflections disappeared (7). As expected, none of the chemical or physical treatments affected the illite peaks, present in all unknown clay samples (5).

2. Cation Exchange Capacity

The CEC values determined for bottom sediment fractions are shown in Table X, and CEC values determined for reference clay minerals

Table IX. X-Ray Characterization of Reference Clays, and Clay Fractions from July 1975 Samples

(d-Spacings in A units)*

Standards	Ch.	Mont.	Il.	Ch.	Kaol.	Il.	Ch.	Qtz.	Kaol.	Ch.	Il.
Kaolinite (API#7)			(9.88wk)		7.37			4.23	3.56		
Montmorillonite		11.90^{c}									
Illite(API#36)	--		9.93	$(7.0)^{a,d}$		4.96	--	4.23		$(3.5)^{a,d}$	
Chlorite**	13.79			7.04			4.70			3.52	
Chlorite-Illite	$13.74^{a,b}$		9.95	$7.03^{a,d}$		4.96	$4.73^{a,d}$	4.30			3.32
Unknowns											
4	$13.79^{a,b}$		9.95	$7.02^{a,d}$		4.98	$4.71^{a,d}$	4.26		$3.53^{a,d}$	3.33
8	$13.74^{a,b}$		9.95	$7.02^{a,d}$		4.98	$4.71^{a,d}$	4.25		$3.53^{a,d}$	3.33
14	$13.71^{a,b}$		9.95	$7.02^{a,d}$		4.97	$4.70^{a,d}$	4.26		$3.53^{a,d}$	3.33
18	$13.73^{a,b}$		9.95	$7.02^{a,d}$		4.98	$4.72^{a,d}$	4.26		$3.53^{a,d}$	3.33

[a] Peak lost on treatment with 6 N HCl at 60°C for 24 hr; characteristic of chlorite.

[b] Increase of peak intensity on heating at 560°C for 1 hr; characteristic of 001 reflection for chlorite.

[c] Expansion of d-spacing (11.90 → 12.47 Å) upon glycolation; collapses to 11.0 Å on heating at 300°C for 24 hr; characteristic of montmorillonite.

[d] Peak lost on heating to 560°C for 1 hr; characteristic of all chlorite spacings except 001 reflection.

** Chemical and physical treatment not done on this chlorite sample.

*$d = \dfrac{1.54}{2 \sin \theta}$, where θ is half the observed 2θ angle.

Table X. Cation Exchange Capacity of Sediment Fractions from Upper Susquehanna Sub-Basin, meq/100 g

Sampling Dates		Sampling Site																	
		4			8 (AP)			14			18 (SB)			CK			CB		
		Sa	Si	Cl	Sa	Si	Cl	Sa	Si	Cl	Sa	Si	Cl	Sa	Si	Cl	Sa	Si	Cl
7/9-11/75	(a)	4.0	6.0	--	3.9	6.7	--	4.8	--	--	4.0	7.4	--	--	--	--	--	--	--
	(b)	4.1	6.0	--	3.8	6.5	--	4.9	--	--	4.1	7.2	--	--	--	--	--	--	--
	Av.	4.0	6.0		3.8	6.6		4.8			4.0	7.3							
11/24-25/75	(a)	4.2	5.1	15.8	2.8	3.3	9.8	4.3	3.5	16.3	3.1	4.5	16.7	4.6	6.1	11.2	1.4	9.2	16.1
	(b)	4.2	6.4	17.3	3.3	6.6	10.2	4.7	3.5	16.0	3.3	4.6	15.7	4.8	7.1	13.0	1.3	9.6	--
	Av.	4.2	5.8	16.5	3.0	5.0	10.0	4.5	3.5	16.2	3.2	4.6	16.2	4.7	6.6	12.0	1.4	9.4	16.1
Site Av:		4.1	5.9	16.5	3.4	5.8	10.0	4.6	3.5	16.2	3.6	6.0	16.2	4.7	6.6	12.1	1.4	9.4	16.1

	Sand	Silt	Clay	Ratio: Sand/Silt/Clay
Sub-Basin Average	3.7	6.2	14.5	1/1.7/3.9
Range	1.4-4.7	3.5-9.4	10.0-16.5	
Rel. Std. Dev.	27%	25%	19%	

are shown in Table XI. The CEC values for the July 1975 and November 1975 samples were similar.

The overall average CEC values for each fraction show that the ratios for sand/silt/clay are 1/1.7/3.9. The relatively low CEC values for sand fractions reflect the mineralogy of sand-sized material (Table VIII). In particular, CB sand which had the lowest CEC value also had the highest quartz content (47.0%). The silt had an intermediate CEC value as compared with the sand and clay. Although no experimental mineralogical examinations were done on the silt material--except one X-ray diffraction analysis on a Gang Mills silt which did show some illite and chlorite clay mineral present--it is believed to be composed of small rock fragments (similar to those in sand, but having a smaller particle diameter) and aggregated clay particles. With this composition, silt would be expected to have a CEC value between sand and clay, and the value 6.2 for silt fractions could represent a mixture of 77% sand-type material and 23% clay-type. The average CEC value for the river clays, 14.5 meq/100 g, is most comparable to that for the reference illite. The CEC results correlate strongly with the % organic carbon in the same samples ($p < .001$) (see Table IV).

Experimental CEC values for the clay minerals range from 6.9 for the heated chlorite to 29.1 for the montmorillonite (Table XI). It is interesting to note that the heated chlorite, with a reddish-brown color that resembles natural clay samples [presumably due to the oxidation of Fe(II) to Fe(III)], had a CEC value only about half that of the green chlorite mineral.

Table XI. Cation Exchange Capacity of Reference Clay Minerals

meq/100 g

Clay Minerals	Trial 1	Trial 2	Av	Literature Values*
Kaolinite #5 (Lamar Pit, Bath, SC)	8.7	8.9	8.8	3-15
Illite (Fithian, Illinois)	14.9	15.4	15.2	10-40
Chlorite (Calaveras Co., CA)	11.9	12.6	12.2	10-40
Heated Chlorite (Calaveras Co., CA)	7.0	6.7	6.8	
Prochlorite (Chester, VT)	18.8	18.3	18.6	
Montmorillonite (Amory, MISS)	28.8	29.4	29.1	10-100

*In D. Carrol (17).

3. Relationship of Element Concentrations to Particle Size

It was pointed out in the previous report (1) and by others (19, 20) that heavy metal concentrations tend to increase as sediment particle size decreases. This can be at least partly explained by the increase in CEC, as shown in the previous section, which reflects not only the increase in surface area per gram (20) leading to greater adsorption, but also differences in mineralogy. Sand-sized quartz particles naturally have less ion exchange capacity than lattice-type clay minerals, which constitute most of the clay and part of the silt fraction (21).

Figure 6 is a log plot of element concentrations for the sand, silt, and clay fractions of two July 1975 samples. It shows not only the range of element concentrations found for each size fraction, but also the tendency for these concentrations to increase on going from sand to silt to clay. The similarity in patterns for the two sites is striking. Data from the four July 1975 samples analyzed by size fractions show that, for most of the trace elements, the average concentrations in sand, silt, and clay are significantly different from one another. This shows the importance of separating sediment into size fractions (or normalizing concentrations to one size fraction as in Section III.A.1) before comparing different samples.

Table XII shows for each element the average concentrations in the sand, silt, and clay fractions for the July and the November 1975 collections. In addition an overall 1975 average is given for each size fraction. In view of the large differences in many November and July values, these overall averages are quite uncertain insofar as they represent average basin samples.

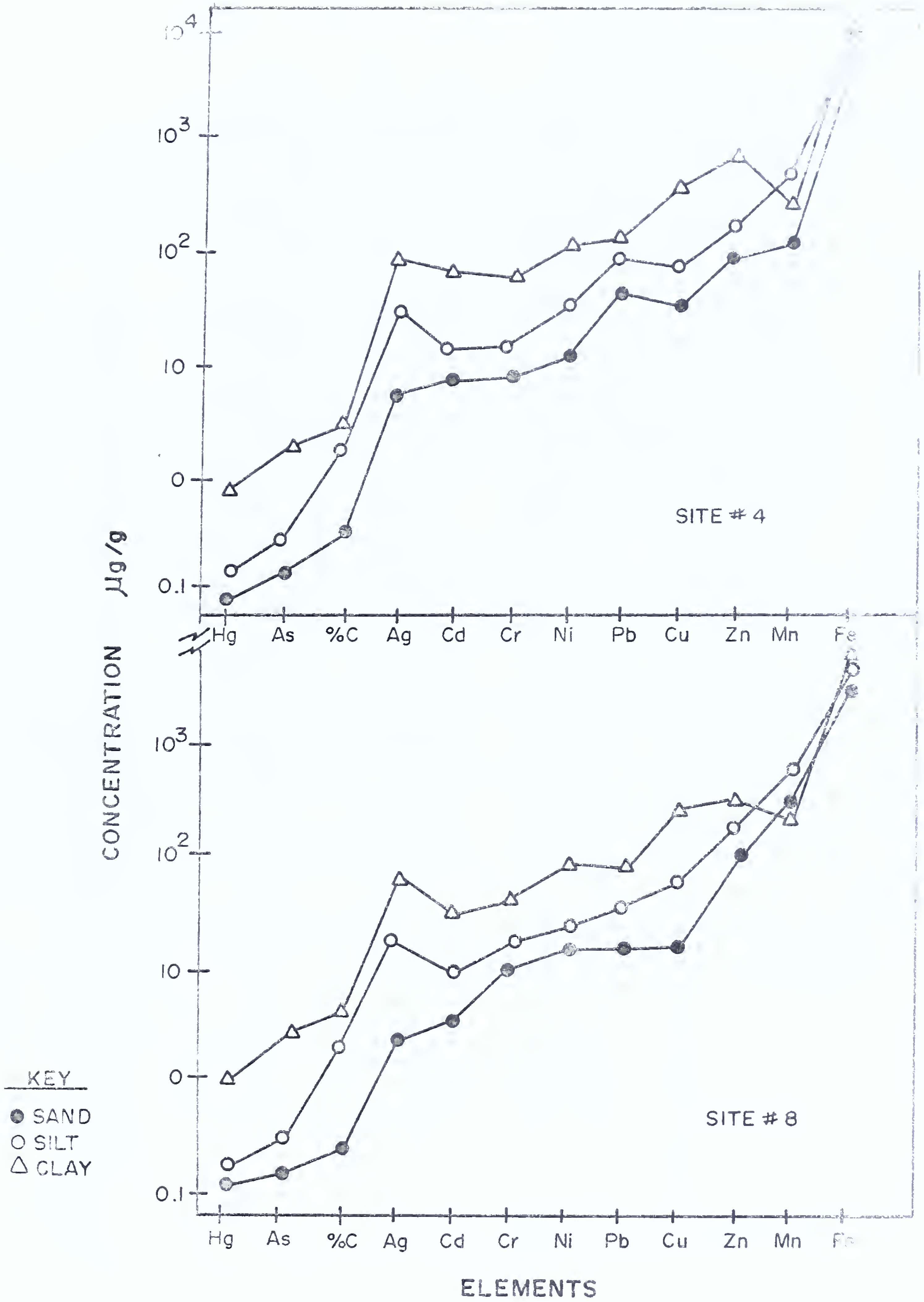

Figure 6. Trends in element concentrations of sand, silt and clay fractions for Sites #4 and #8, July 1975.

Table XII. Average Element Concentrations in Sand, Silt, and Clay Fractions

from 1975 Collections in Upper Susquehanna River Sub-Basin

Sample Code[a]	Av. Concentrations, in µg/g (unless otherwise noted), ± Std. Dev.											
	Ag	As	%C	Cd	Cr	Cu	Fe (mg/g)	Hg	Mn	Ni	Pb	Zn
Sand												
July (4)	3.2±1	0.22±.04	.29±.06	2.9±2	7±2	20±4	9±1	.064±.02	286±71	16±4	25±11	73±11
Nov. (5)[b]	1.6±1	0.23±.02	.78±.15	1.0±1	4±2	11±3	5±1	.036±.03	342±99	9±2	24±13	37±7
Average[c]	2.4	0.22	.54	2.0	6	16	7	.050	314	12	24	55
Silt												
July (4)	13±10	0.34±.05	1.97±.23	12±6	12±2	77±15	7.9±1	.171±.02	593±342	26±3	46±11	109±10
Nov. (6)	5.2±4	0.36±.08	1.75±.28	2.7±2	8±3	28±8	9.9±2	.098±.02	477±125	19±4	28±6	72±16
Average[c]	9.4	.35	1.86	7.6	10	52	8.9	.134	534	22	37	90
Clay												
July (4)	97±59	2.7±.9	3.86±.29	28.9±19	38±10	419±97	10±2	.87 ±.29	302±94	132±32	110±28	416±81
Nov. (6)	16±8	2.77±.54	3.26±.82	5.6±5.5	30±7	86±33	30. ±4	.47±.07	1121±476	61±5	<100	157±14
Average[c]	56	2.7	3.56	17	34	252	20	.670	712	96	<105	286

[a] No. of samples averaged shown in parentheses.

[b] The Site #4 sand fraction was anomalous, and therefore was omitted from the November average.

[c] Arithmetic mean of July and November averages.

The concentration ratios for the fractionated samples collecte in 1975 are shown in Table XIII.* One could have used the average elemen concentrations in each size fraction (Table XII) to calculate sand/ silt/clay ratios, but due to the spatial and temporal fluctuations in values it seemed advisable to calculate a sand/silt/clay ratio for each sample and then average these ratios to get the July, November, and overall average ratios. Although the concentrations changed drastically in many cases before and after Eloise, there was much less change in the sand/silt/clay concentration ratios for most of the trace metals. (A change by a factor of >2 in at least one ratio did occur for Ag, Cu, Fe, Mn, and carbon.)

The overall average element concentration ratios are depicted in Figure 7.* This shows that four elements with high ratios (Ag, Cd, Cu, Hg) which have earlier been shown (Figures 3 and 4) to be associated with pollution, concentrate more in the silt and clay than in the sand fractions, compared to other elements. The high clay/sand ratio for As may be related not to pollution, but to the anionic nature of this element.

Taking all the elements of Table XIII, the median sand/silt/clay ratios are 1/2.2/7.9. The median ratios for the July 1975 and November 1975 samples were surprisingly close, 1/2.4/9.6 and 1/2.2/7.1, respectively, demonstrating that the ratios did not change significantly even though the concentrations were much different. Considering only eight surficial HM's [As, Cd, Cr, Cu, Fe, Ni, Pb, Zn] determined both in 1974 and in 1975, the median ratios for 1975 were 1/1.8/7.2, lower than the corresponding ratios of 1/3.3/12 calculated for 1974.

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*The sand and silt fractions, if separated using the USGS basis, would each be somewhat higher in HM's; the silt/sand ratio thus might not be changed much from the above, but the clay/sand ratio would be lower.

Table XIII. Ratios of Element Concentrations in Sand/Silt/Clay Fractions from 1975 Collections[a]

Site	Ag	As	%C	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
July '75												
4	5.2/33	1.6/12	4.8/11	3.7/10	1.9/7.3	2.6/15	0.8/1	2.4/12	1.5/1.2	1.3/7.2	1.2/4	1.5/5.8
8	4.8/25	1.5/12	7.5/4	3.4/10	1.4/4.4	3.3/6	0.8/1	1.3/12	1.3/0.8	1.4/6.2	2.5/5	1.3/4.7
14	9.0/20	1.5/17	9.4/22	9.0/20	1.6/6.6	6.6/39	0.7/6	4.3/20	2.9/1.1	1.5/10.7	3.6/5	2.3/7.7
18	5.6/19	1.5/9	6.8/10	6.3/4	3.3/6.3	4.1/17	1.3/1	5.4/12	2.1/1.1	2.5/8.9	2.1/5	1.7/4.7
Average	6.2/24	1.5/12	7.1/12	5.6/11	2.1/6.2	4.2/19	0.9/2	3.4/14	1.9/1.1	1.7/8.3	2.4/5	2.3/5.7
Std. Dev.	1.7/5	0.0/3	1.6/10	2.3/6	0.7/1.1	1.1/12	0.2/2	1.6/4	0.6/0.2	0.5/1.7	0.9/1	1.4/1.2
Nov. '75[b]												
8	13.3/23	1.4/13	3.2/4.3	11/7.5	0.7/2	3.9/12	2.5/8	5.1/15	1.9/1.5	2.5/6.8	1.9/2	2.3/3.8
14	1.4/14	2.4/14	1.4/4.6	1.4/6.7	1.0/6	0.8/7	1.0/6	0.8/6	0.6/3.5	1.3/6.4	0.9/4	1.2/4.1
18	4.0/7	1.6/11	2.5/4.9	3.7/6.9	1.5/5	2.4/8	1.2/4	4.4/18	1.8/5.5	1.4/5.1	1.6/6	1.6/3.2
CK	1.9/10	1.9/7	2.2/3.2	1.6/7.6	3.0/16	2.0/9	3.0/8	4.7/35	1.1/1.3	2.4/9.0	1.0/19	3.0/6.1
CB	1.1/2	1.2/15	2.1/4.8	0.8/15	1.4/7	5.3/3	2.3/5	7.1/36	1.6/3.5	3.1/8.8	0.6/2	2.0/4.3
Average	4.3/11	1.7/12	2.3/4.4	3.7/8.7	1.5/7	2.9/8	2.0/6	4.4/22	1.6/3.1	3.2/7.2	1.2/7	2.0/4.3
Std. Dev.	4.6/7	0.4/3	0.6/1	3.7/3.2	0.8/4	1.6/3	0.7/2	2.0/12	0.6/1.5	1.7/1.5	0.5/4	0.6/1.0
Overall Average[c]	5.1/18	1.6/12	4.4/8	4.5/9.7	1.8/6.7	3.4/14	1.5/4	3.9/18	1.6/2.1	2.5/7.8	1.7/6	1.9/5.0

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[a] First number shown of each pair is the silt/sand ratio of concentrations; second number is the clay/sand ratio.

[b] The ratios for Site #4 are omitted, because of the unusual nature of the #4 sand fraction.

[c] Arimetic mean of the July '75 and Nov. '75 averages.

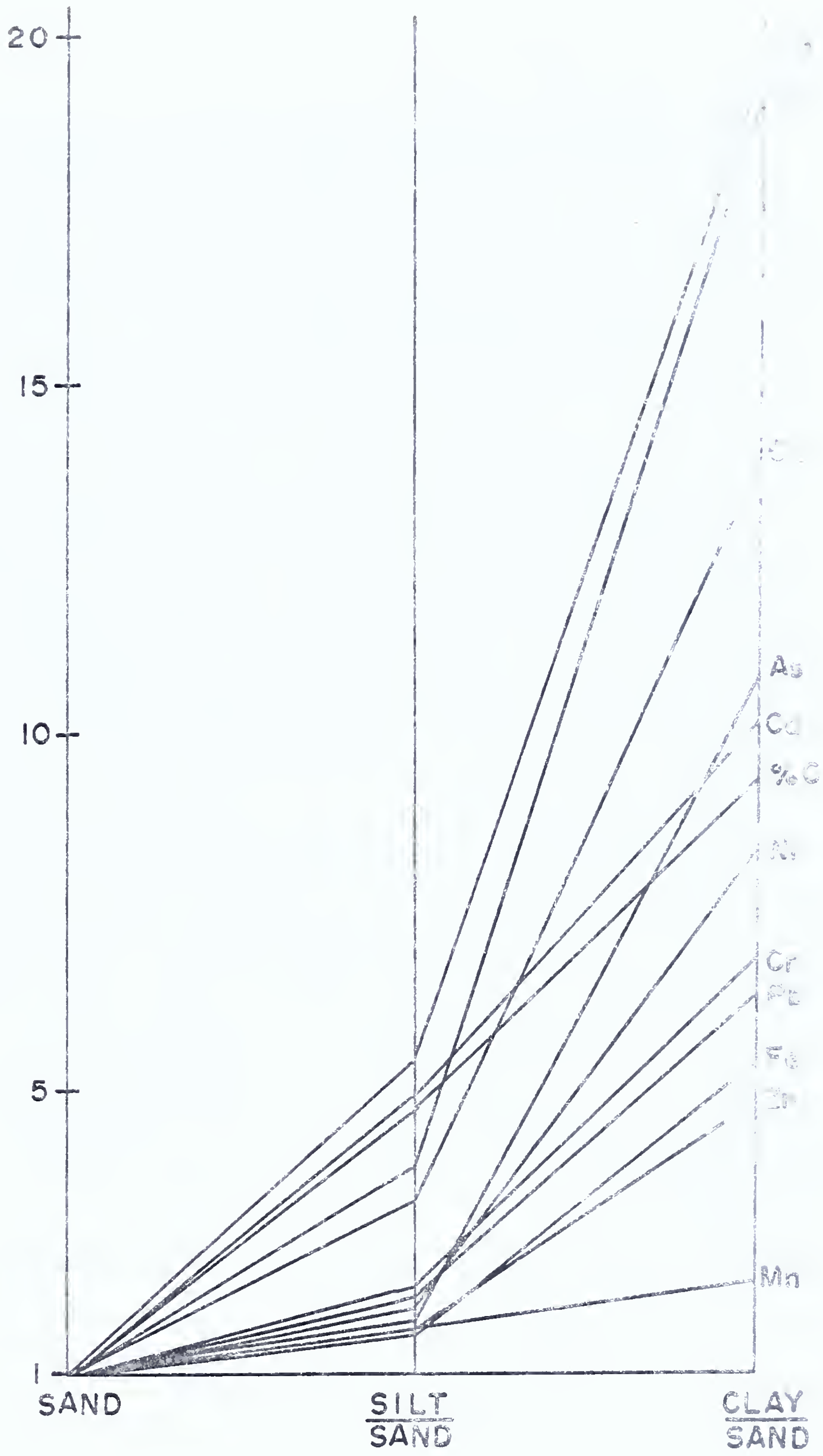

Figure 7. Average concentration ratios in sand/silt/clay fractions for each of twelve elements.

Excluding As and C, which are not cationic in nature, the median overall ratios for 1975 were 1/2.2/7.2. These can be compared to the CEC ratios for sand/silt/clay of 1/1.7/3.9. The agreement in silt/sand is close, and in clay/sand is within a factor of 2. Thus it appears that differences in CEC can explain a large part, but not all, of the HM size distribution in sediments. [The distribution of "surficial" Fe is definitely not by a CEC mechanism, since the concentrations of Fe found exceed by about a factor of 10 the amounts equivalent to the CEC for sand, silt, and clay fractions. Probably the Fe is present as hydrous ferric oxide, and some may even be dissolved from the clay matrix by the "surficial" digestion process in a partial decomposition of the clay mineral (22).]

The concentrations in the size fractions of this study are of the same order of magnitude as those found from other studies in comparable size fractions, (Table XIV), differing by a factor of 3 or more only for Hg, Mn, and Pb in sand and Cr, Fe, and Hg in clay. The agreement in the sand and the silt fractions is surprising in view of the fact that the leaching method in the Canadian study was relatively drastic (digestion in 4 M HNO_3 +0.7 M HCl for 2 hr at 70-90°C). However, compared with the present study, the silt to sand ratios for the Canadian study are higher in all cases, except for Pb which is approximately equal to the present work and Hg which is lower. The relatively high silt/sand concentration ratios in the Canadian study may be due to their use of finer silt and coarser sand particles.

Table XIV. Comparison of Element Concentrations in SRB-NYS Sand, Silt, and Clay to Results from Other River Sediment Studies

	Heavy Metal Concentrations*								
Material	Sand		Silt		Clay			Silt/Sand Conc. Ratios	
	Ottawa & Rideau R. (26)	Present Work**	Ottawa & Rideau R. (26a)	Present Work**	German Rivers, Av. of four (32)	Tennessee Rivers, Av. of four, (55)	Present Work**	Ottawa & Rideau R.	Present Work***
Particle Size	(2-0.5 mm)	(2-0.25 nm)	(0.062-0.004mm)	(0.25-0.004mm)	(<.002)	(<.00015 mm)	(<.004 mm)		
Element									
Cd	--	2.0	--	7.6	11	18	17	--	3.8/1
Cr	9.	6.	27.	10.	115	--	34	3.0/1	1.7/1
Cu	9.	16.	25.	52.	180	400	252	2.8/1	3.3/1
Fe(mg/g)	4.3	7.	17.4	8.9	--	2.3	20	4.0/1	1.3/1
Hg	0.15	0.050	0.22	0.134	2.7	--	0.67	1.5/1	2.7/1
Mn	63.	314.	189.	535.	--	1400	712	3.0/1	1.7/1
Ni	10.	12.	29.	22.	106	70	96	2.9/1	1.8/1
Pb	5.	24.	33.	37.	150	180	105	6.6/1	1.5/1
Zn	24.	55.	88.	90.	600	500	286	3.7/1	1.6/1

*Concentration as µg/g (dry wt.) except for Fe.

**Overall average concentrations from Table XII.

***Calculated from average values presented in this Table.

4. Organic Matter and Humic Substances in Sediments

Total organic carbon in the 22 downstream samples averaged 1.15%, ranging from 0.5 to 20%. [Four of these samples analyzed by size fractions (#4, 8, 14 and 18) averaged 1.12% C for the whole samples, but the weighted averages of the fractional analyses gave only 0.54% C, indicating that much organic matter (oil or grease?) was lost in the process of size fractionation.]

Analysis of the sand, silt, and clay fractions gave average % C concentrations of 0.29, 1.97, and 3.86, respectively, for July 1975 and 0.78, 1.75, and 3.76, respectively, for November 1975 (excluding the anomalous #4 sand fraction). A number of these samples were also analyzed for humic acid (HA) and fulvic acid (FA) using the alkaline extraction-spectrophotometric method of Schnitzer and Khan (23).* In general, the HA/FA absorbance ratio was about 7/1. The average results for % HA are shown below (with number of samples analyzed in parentheses):

	July 1975	November 1975
Sand	--	0.07 (2)
Silt	0.11 (4)	0.15 (6)
Clay	--	0.42 (2)

From the November 1975 results, assuming that HA is about half carbon, one calculates that HA represents only about one-twentieth of the total organic carbon in these size fractions.

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*The analyses for humic substances were done by Francis Emmi, in an undergraduate independent work project.

This small amount of HA-carbon in sediments may nonetheless be significant. Typical soil HA has an acid exchange capacity of ∿8 meq/g (23). Using this factor, one calculates that HA in the November 1975 size fractions could account for ∿20% of the observed CEC for those samples.

C. COMPARISON OF SUSQUEHANNA RIVER SEDIMENTS FROM NEW YORK STATE WITH OTHER RELEVANT MATERIALS

The all-site median concentrations (Table VII) from the Susquehanna River Basin in New York State (SRB-NYS) are compared in Table XV with available data for extractable metals in other river sediments, estuary sediments, and related materials.

The results of the present study compared to average data for the entire Susquehanna River Basin (SRB) show that the latter sediments are approximately twice as high as those of SRB-NYS, with Pb being even higher. Although the size distribution was different (much more clay and less silt in the samples from the entire Basin) this would not explain such elevated concentrations. Chesapeake Bay sediments are higher in most metals than the SRB-NYS sediments and generally greater than or equal to the average concentrations for the entire Basin, except that Pb was 10X lower in Bay sediments than in the entire-Basin samples.

Data for U.S. and Canadian rivers are similar to those of the present study. For example, the mean values for the Ottawa and Rideau River sediments in Canada and the data for SRB-NYS agree in Cd, Cu, Ni, Zn, and Fe, but the Canadian sediments are somewhat

Table XV. Comparison of SRB-NYS Sediments with Other Relevant Materials

Location, Method and Material	Element Concentrations, μg/g (averages unless otherwise noted)												
	Ag	As	%C	Cd	Co	Cr	Cu	Fe (mg/g)	Hg	Mn	Ni	Pb	Zn
Susq. R. & Chesapeake Bay													
Present study, SRB-NYS, 1974 & 1975; H_2O_2 + 0.3 M HCl; <2 mm; medians	2	0.31	0.48	0.4	--	4	13	9.6	0.019	328	18	21	64
SRB, 1974; H_2O_2 + 0.3 M HCl; 25 stations; <2mm; (24)	6	9 (total)	--	1	19	12	35	14.3	0.06 (total)	635	19	123	154
Chesapeake Bay, 1974; warm HNO_3; no size given; (25)	--	--	--	0.9	--	25	20	39	--	690	26	27	128
U.S. & Other Rivers													
Ottawa & Rideau 1970; 4 M HNO_3 + 0.7 M HCl; <2+ mm, ground; (20)	--	--	--	--	12	22	26	11	0.24	180	22	34	85
Ottawa & Rideau 1972; as above, except size <.18 mm; (26)	--	--	--	0.46	18	41	23	28	0.46	454	24	54	128
Meramec Park Basin, Missouri,1974; hot conc. HNO_3; <.18 mm; (27)	--	3.1	--	1.3	--	--	31	--	Trace	--	12	84	71
Illinois R. in Peoria, Ill., 1973; conc. HNO_3; silt; one sample; (28)	--	5	--	3	6	64	22	--	0.12	--	22	64	185
Three E. Georgia Rivers, 1974; 0.1 M $NH_2OH \cdot HCl$ + 0.1 M HNO_3; <.18 mm (29)	--	--	--	--	10	--	40	2.2	--	200	--	30	90

Table XV. (Cont'd)

Location, Method and Material	Element Concentrations, μg/g (averages unless otherwise noted)												
	Ag	As	%C	Cd	Co	Cr	Cu	Fe (mg/g)	Hg	Mn	Ni	Pb	Zn
Three Rivers in Israel, 1973; 1 M NH_2OH and 25% OAc; <.18 mm; (30)	0.1	--	3.3	--	54	12	2.3	--	0.46	--	9	12	44
Estuaries													
Pamlico (N.C.), 1973; 5% H_2SO_4 & 5% HNO_3; sand-silt (31)	--	--	--	4	10.1	35	11	--	--	--	39	14	31
Elbe Germany, 1973; leaching procedure not given, <2μm; (32)	--	--	--	15	45	176	44	--	2.1	--	56	152	459
Suspended Solids													
Susq. Basin near Binghamton, N.Y.; 1974; total conc; 4 stations, av. medians (14)	--	--	--	21	34	128	175	--	--	--	150	278	1020
Cayuga Lake Basin, N.Y., 1970; total conc; (33)	--	--	--	16	12	--	570	--	--	--	--	484	1044
Rhine R., Netherlands, 1970; total conc; <.016 mm sediments or susp. solids (34).	--	220	--	45	--	1240	600	--	23	--	100	800	2900
Soils and Shale													
Soils in NYS (35)	--	--	--	0.2	9	--	22	--	--	--	--	7.9	80
Shales in Pennsylvania (36)	--	--	--	--	6	144	--	--	--	--	60	--	--
World Shales (37)	--	1.3	--	0.3	19	90	45	--	0.4	--	68	20	95

higher in Pb and distinctly higher in Cr and Hg. (The 1972 Ottawa and Rideau River sediments may be higher than the 1970 results for the same rivers because of a smaller average particle size in the 1972 study.)

Sediments from rivers in Missouri and Illinois were higher in most elements than those of the SRB-NYS, possibly because a more drastic leaching procedure was used, but they were comparable in most elements to the SRB results. Analyses from Georgia rivers were comparable to the SRB-NYS data. Sediments from rivers in Israel, subjected to a mild leaching agent ($NH_2OH + OAc^-$), were high in % C, Cr and Hg, compared to SRB-NYS data, suggesting specific pollution inputs. (The Israeli rivers were shallow and slow moving, accounting for the high % C.)

The geochemistry of a region may be expected to affect the "natural" sediment concentrations. Thus it is interesting that a variety of river sediments from this country and abroad, subjected to different leaching methods, yield such similar results: the data of Table XV cover more than a 10-fold range only for 5 out of 12 HM's (Ag, As, Cr, Cu, and Hg), all of which are often associated with pollutional inputs. If the Israel data based on mild leaching conditions is omitted, the narrowness of the ranges is even more striking. One might conclude that the aquatic chemistry of HM's influences bottom sediment concentrations as much as or more than geochemical background, except in special circumstances (e.g., near mercury mines).

Suspended solids in the Susquehanna River near Binghamton, similar in elemental concentrations to those for streams of the Cayuga Lake Basin, had concentrations ∿20X higher than for the SRB-NYS sediments. This is related to the fact that suspended matter at times of normal flow is mostly fine clay. For comparison, data on <.016 mm sediments from the polluted Rhine River in the Netherlands are included.

Upstate New York soil samples had mean total concentrations of Cd, Cu, Pb, and Zn that were quite close to those of SRB-NYS sediments. This is significant, since soils in this region contain much higher fractions of clay and silt than do the river bottom sediments; these abundant soil fractions (of higher surface area) apparently are not as rich in elemental concentrations as the corresponding sediment fractions which have been exposed to river water, otherwise the overall elemental concentrations in soil would be much higher than in bottom sediments.

Pennsylvania shales from the Wyoming-Lackawanna Valley were much higher in Cr and Ni, but lower in Co concentration, than SRB sediments. In general the total concentrations in world shales are the same or somewhat higher than the surficial concentrations for SRB-NYS sediments, except for Cr and Hg which are much higher in shales.

Comparison of Heavy Metals in Street Dirt and Bottom Sediments. A study of the toxic materials in street contaminants from four U.S. cities (San José, Seattle, Baltimore, and Tulsa) was done recently by Pitt and Amy (38), using 6 M HCl to leach HM's from various size fractions. It is interesting to compare their results with the river sediment data of this study.

In street dirt, the concentrations in the silt and fine sand fraction (<.104 mm) were about 2 to 3X higher than in the medium and coarse sand fraction for Cd, Cr, Cu, Ni, Pb, and Zn, and about the same in the two fractions for Fe and Mn. These approximate the silt/sand ratios for HM's in bottom sediments.

Comparing street dirt to bottom sediment, the concentrations in dirt (silt and fine sand fraction; 6 M HCl digestion) were roughly the same as in the July 1975 silt fractions downstream from Binghamton (surficial digestion) for Cd, Mn, and Ni, but higher in street dirt for many elements: ∿5X for Cu, Fe, and Zn; 10X for Pb;* 40X for Cr. Undoubtedly the high Pb in street contaminants is from leaded gasoline exhaust, and presumably the high Cr, Fe, and Zn are from automotive traffic (chrome plating and iron; Zn compounds in tires), but the source of the elevated Cu in street dirt is not readily apparent, unless it is from copper wires and scraps of brass.

D. MECHANISM AND MAGNITUDE OF HEAVY METAL TRANSPORT IN RIVERS

Having examined in some detail the nature of river bottom sediments from various areas and at selected times, and in particular the HM concentrations in three size fractions of the sediments, one then attempts to understand the mechanisms through which such HM concentrations are established, and their relationship to river transport.

As mentioned previously, the increase in CEC on going from sand to clay may be responsible for part of the buildup in HM concentration, reflecting the increased surface area and changes in mineralogy.

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*Street dirt collected in 1975 along NY Rt. 434 near the Binghamton-Vestal town line gave the following surficial Pb results: sand 574, silt 980, clay 1980 μg/g; <1 μg/g soluble in the seiving water.

1. Element-Element Correlations

Association with organic matter, and adsorption on Fe and Mn oxide coatings, are two mechanisms often used to explain trace metal uptake by soil and sediment particles. Thus, data from the 1975 sediment study have been examined by linear regression analysis to establish the degree of element-element correlation among the various samples.

Correlation coefficients for pairs of parameters from the 22 downstream samples of July 1975 are given in Table XVI; the top matrix is from the whole-sample analyses of Table III, the bottom is based on normalized concentrations calculated for the sand fractions alone, which adjusts for the varying particle-size distribution in the 22 samples (see Appendix A).

For the whole samples, only about a third of the element-element pairs showed significant correlations. Silver had a very strong correlation with Cd, and As correlated very strongly with Cr (and with river miles downstream). Copper had a very strong positive correlation with % C and a strong correlation with Ag and with Cd. Total organic carbon (%C) had a very strong positive correlation also with Cr and with % silt and a very strong negative correlation with % sand; % C also had a strong correlation with As, and a medium correlation with Ag and % clay. There were no significant correlations for Mn, and only one medium correlation for Hg (with Cu).

For the normalized sand concentrations, the element-element correlations were even fewer. The correlations found for % C with Ag, As, and Cu in the whole samples were no longer significant.

Table XVI. Correlation Coefficients for Sample Parameters from 22 Downstream Sites[a]

	As	%C	Cd	Cr	Cu	Hg	Mn	%Sand	%Silt	%Clay
Based on Whole-Sample Analyses										
Ag	.02	.47†	.86**	.19	.58*	.29	-.13	-.43†	.40	.22
As		.60*	-.07	.67**	.24	-.30	.23	-.50†	.38	.24
%C			.28	.64*	.69**	.23	-.13	-.91**	.83**	.50†
Cd				.08	.54*	.07	.01	-.27	.23	.20
Cr					.16	-.01	.07	-.26	.19	.16
Cu						.42†	.01	-.65**	.57*	.34
Hg							.23	-.22	.20	.08
Mn								.09	-.17	.09
Based on Concentrations Calculated for Sand Fractions										
Ag	-.02	.18	.87**	.05	.42†	-.09	-.16			
As		.25	-.15	.07	-.06	.05	-.28			
%C			-.02	.56*	.26	-.04	-.45†			
Cd				-.01	.47†	-.22	.01			
Cr					-.03	-.13	.05			
Cu						.12	-.01			
Hg							-.16			

[a] Correlation Coefficients and Probabilities:
r = .65 (p = .001, very strong)**
r = .53 (p = .01, strong)*
r = .42 (p = .05, medium)†

However, the very strong correlation for Ag with Cd remained. The correlations of % C with Cr and of Cu with Ag and Cd were still significant although weaker, and a medium negative correlation appeared for % C with Mn.

As indicated previously, four of the July 1975 samples and the six November 1975 samples were analyzed by size fractions. In Table XVII the correlation coefficients for the sand fractions alone (excluding the anomalous November 1975 sand at site #4), the silt fractions, and the clay fractions are shown. All three separate* coefficient matrices are placed in one table to facilitate comparison among the different size fractions.

Generally, the size fractions analyzed separately gave few very strong or strong correlations, with practically no significant correlations for As, % C, Cr, and Mn and relatively few for Fe, Pb, and Hg. [There were twice as many very strong element-element correlations in the clay as in the silt, with the sand correlations intermediate. This may be indicative of the relative purity in mineralogy for the clay fractions as compared to the sand and silt materials.] Silver was very strongly correlated with Cd, and Ni with Zn, in all three size fractions of the sediments. Zinc had a strong correlation with Ag and Cd, and Cu tended to increase in its correlation coefficient with Zn and with Ni from sand-to-silt-to-clay.

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*If analyses for sand, silt, and clay fractions are all compared in one matrix, biased coefficients are obtained which show very strong apparent element-element correlations.

Table XVII. Correlation Coefficients for Separate Sand, Silt, and Clay Fractions of 1975 Samples[a]

	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	%C
Ag	-.78†	.96**	.62	.87*	.63	.59	-.36	.90**	.34	.82*	-.52
	-.37	.98**	.58	.46	-.45	.64†	-.10	.34	.62	.80*	.04
	-.10	.96**	.14	.68†	-.68†	.57	-.50	.87**	.78*	.88**	.38
As		-.81*	-.65	-.56	-.33	-.69†	.23	-.70†	-.32	-.52	.10
		-.37	-.31	-.18	-.45	-.05	-.12	-.62	-.39	-.59	-.54
		-.20	-.14	.19	-.12	-.13	.11	.80*	.14	.10	.53
Cd			.58	.79†	.59	.53	-.39	.91**	.35	.83*	-.51
			.04	.58	.50	.68†	.00	.71†	.72†	.84*	.09
			.78*	.59	-.65†	.68†	-.20	.55	.67†	.83*	.34
Cr				.57	.73†	.87*	-.43	.72†	-.02	.66	-.39
				-.13	.08	-.05	.00	.05	.10	.04	.10
				.40	-.33	.69†	-.64†	.93**	.48	.63	.44
Cu					.64	.69†	-.30	.77†	.00	.77†	-.59
					-.03	.85*	.57	.73†	.82*	.78*	.56
					-.89**	.64†	.67†	.92**	.40	.93**	.38
Fe						.57	-.30	.85*	.00	.84*	-.85*
						-.40	.07	-.04	-.36	-.13	.52
						-.62	-.47	.64†	-.33	.91**	-.52
Hg							-.35	.60	-.17	.60	-.34
							.28	.71†	.63†	.77*	.45
							-.47	.61	.07	.73†	.38
Mn								-.35	.01	-.57	.36
								.14	.67†	.22	.28
								-.61	-.13	-.61	.04
Ni									.19	.89*	-.72†
									.62	.93**	.70†
									.63†	.98**	.51
Pb										.17	.26
										.76	.26
										.56	.23
Zn											.80*
											.58
											.49

[a] Sand fractions (1st row for each element): r = .90 (p = .001**), r = .80 (p = .01*), r = .67 (p = .05†).
Silt and clay fractions (2nd and 3rd rows, respectively): r = .87 (p = .001**), r = .76 (p = .01*), r = .63 (p = .05†).

In view of the common observations that trace metals bind to organic C or adsorb on Fe and Mn oxide coatings, it is surprising that there were no strong positive correlations between the trace metals and either % C or Mn, and few correlations for Fe. In the case of % C, the positive correlation with some trace metals in unfractionated samples and the lack of correlation among samples of a given size fraction indicates that, as average particle size decreases, both % C and metals such as Cu increase, perhaps due to adsorptive forces, but not because the elements are associated with one another. In the case of Fe and Mn the thickness of an oxide coating may be quite variable, thus the lack of correlation between Fe or Mn and other trace metals, within a size fraction, is not surprising and does not rule out adsorption on the oxide coating as an important uptake mechanism.

Whitney (56) examined size fractions for a number of different sediment samples. For each sample, he found a strong correlation for citrate-leachable Cd, Pb, and Zn with Mn and Fe, among the various size fractions (pebbles to silt) of that sample. However, from his data, and from our work, it appears that correlations among different size fractions of an individual sample are stronger than correlations among different samples within a given size fraction. The exception in our case (strong correlations for Ag, Cd, Cu, Ni, and Zn within the various size fractions) may be evidence for a cation exchange mechanism and common pollutional sources.

2. Uptake and Release of Cd(II) and Pb(II) by Sediment Materials (14)

An adsorption isotherm for Cd(II) on the NSS material, from synthetic RW at 25°C, is shown in Figure 8. The low concentration

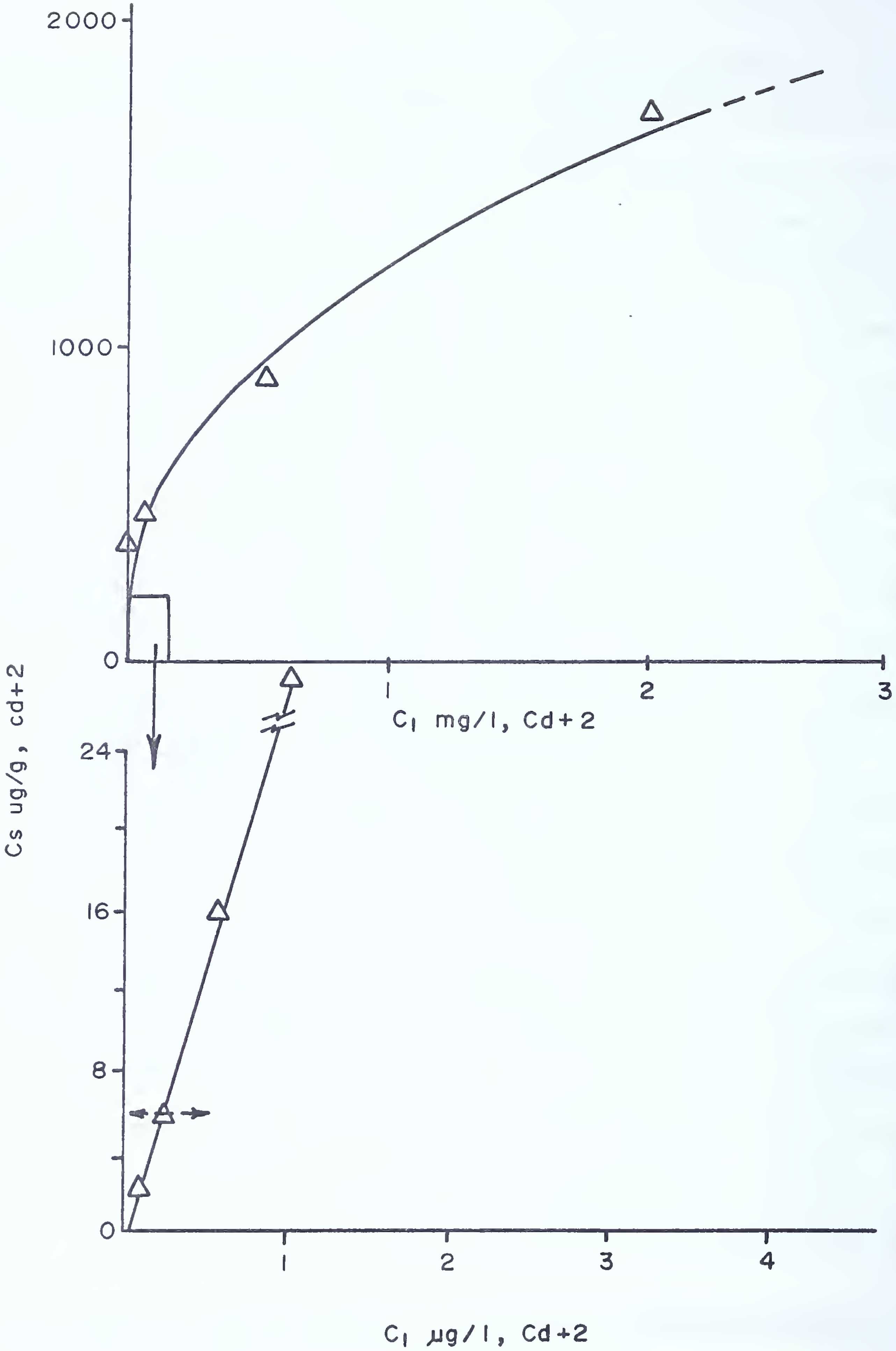

Figure 8. Adsorption isotherm for Cd(II) on Natural Suspended Solids, from synthetic river water medium at 25° C. (Expansion of curve below shows low concentration data.)

detail, typical for Cd(II) and Pb(II) on all the solids tested, shows that these metals are taken up from solution effectively by sediment materials, tending to "buffer" the solution at relatively low metal concentrations. Thus the natural concentrations of soluble Cd(II) and Pb(II) in RW do not fluctuate widely, if the water is in contact with sediment of uniform concentration (14). However, metal inputs from pollution can raise the metal concentrations in both sediment and water, and the presence of solubilizing ligands can increase the fraction of total metal in solution.

The adsorption isotherm data for Cd(II) and Pb(II) on sediment materials are presented in Figure 9a and 9b, respectively, as Freundlich-type log-log plots. Three of the materials (API illite, Chenango R. illite-chlorite mixture, and the NSS silt/clay mixture) behaved similarly; uptake on the California chlorite was favored ∿10 fold, at low solution concentrations.

Also shown in Figs. 9a-b are the data patterns for Cd(II) and Pb(II) in storm samples taken in May and September, 1974, at times of relatively high river flow (14). These data show that the relationships between insoluble and soluble Cd and Pb are comparable to those obtained _in vitro_ using synthetic RW and sediment materials; apparently much of the total Cd and Pb of suspended solids is adsorbed, as suggested by Kennedy (21).

The slopes of the Cd curves are near unity at low concentrations, indicating proportional uptake, in agreement with the data of Gardiner on river mud (39). From data on the Cd and Ca concentrations in solution and on the solid at equilibrium, a selectivity coefficient, K_{Cd}^{Cd}, of 550 was calculated for illite (14). The Pb curves at low

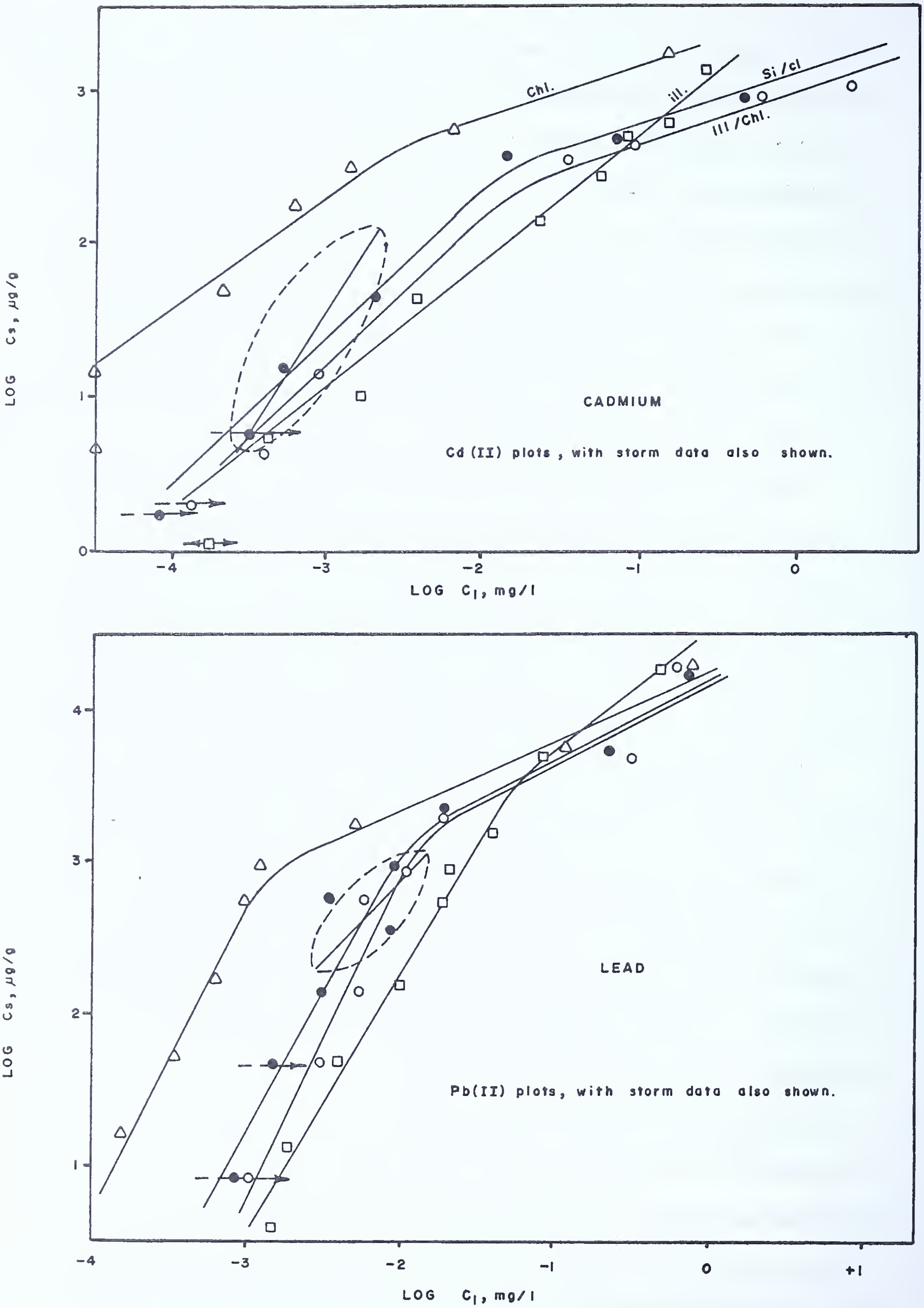

Figure 9. Freundlich plot, log C_s vs log C_l, for Cd(III) and Pb(II) on sediment materials, at 25°C (14).

concentrations have slopes from 1.7 to 2.0, which could indicate that Pb_2OH^{3+} or other polynuclear Pb-species are the predominate solid or adsorbing species. The formation constant of Pb_2OH^{3+} is $10^{7.7}$, from a recent compilation (40), so it is not a predominate solution species at pH 7.5.

In Figure 10 the uptake of Cd and Pb on illite, a predominant clay mineral in this region, is compared with the curves obtained for $HgCl_2$ and CH_3HgCl by Reimers and Krenkel (41,42). Although Pb is taken up more strongly than Cd at high concentrations, the curves cross at low concentrations comparable to many RW samples. The fact that Pb and Cd are adsorbed more strongly than both Hg species* may indicate that an ion exchange mechanism is operating in the former cases, whereas the predominant Hg species are neutral molecules.

The release of Cd and Pb from metal-rich sediments prepared in the laboratory gave the following results (see Table XVIII): in synthetic RW, both metals were only partially released, Cd > Pb; in RW at pH 3.0, both were released ∿100%; in sea water, Cd, was released 100% and Pb only partially. These data have interesting environmental implications with respect to the behavior of trace metals when loaded sediments encounter acid mine drainage or sea water.

River water containing nitrilotriacetic acid (NTA), a detergent substitute with chelating properties for metal ions, was much more effective at releasing Cd than Pb, except from the chlorite mineral. And concentrated Mg^{2+} solutions "desorbed" Cd(II) 100%, but Pb(II) was only partially released (except, again, for the anomalous behavior of California chlorite).

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*However, note that the SRB-NYS data for Hg (in clay 0.6 μg/g; dissolved 0.03 μg/ℓ) fit the Cd(II) line better than the $HgCl_2$ line.

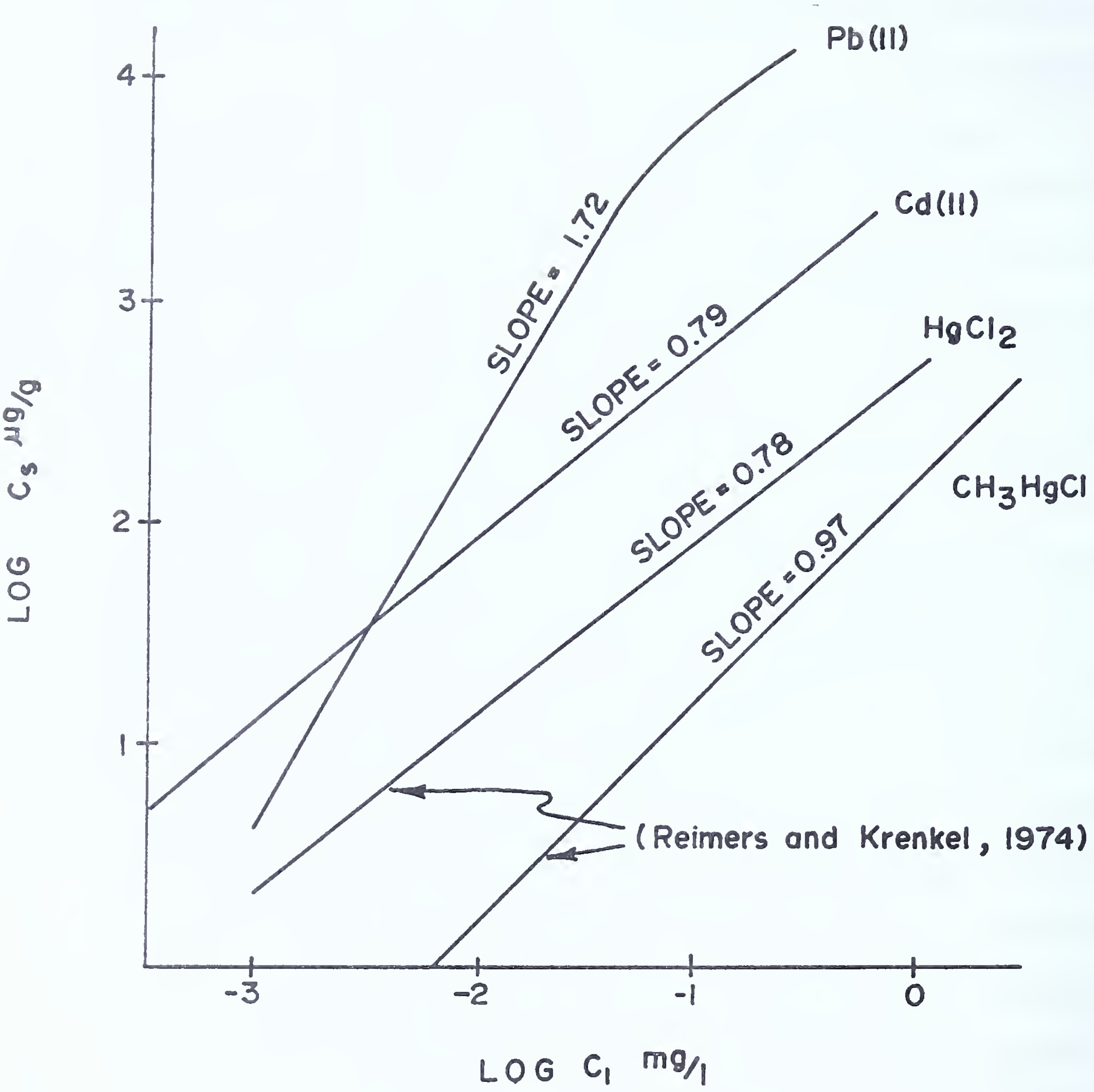

Figure 10. Comparison of adsorption isotherms for Cd(II), Pb(II), $HgCl_2$, and CH_3HgCl on illite (41; mercury data from reference 42).

Table XVIII. Release of Cd(II) and Pb(II) from Pre-Enriched Sediment Materials.*

Media	Initial pH		Materials and % Release of Cd and Pb			
			Clay	Chlorite -Illite	Calif. Chlorite	API #36 Illite
Synthetic River Water (RW)	7.5	Cd:	22	35	44	34
		Pb:	5	7	28	17
Acidified RW	3.0	Cd:	103	102	103	103
		Pb:	122	113	108	100
Syn. RW + 1.0 mg/ℓ of NTA	7.1	Cd:	103	107	62	66
		Pb:	16	9	114	18
Syn. Sea Water	7.7	Cd:	114	103	106	103
		Pb:	10	19	48	18
Strong Electrolyte						
1.0 N $MgCl_2$	7.0	Cd:	113	103	111	103
1.0 N $Mg(NO_3)_2$	7.0	Pb:	14	10	101	27

[*] The materials were loaded initially either with ∿1.1 μg Cd or with ∿8.7 μg Pb, per 25 mg of sediment material. Volume of release medium was 50 ml in each case. Results above 100% may reflect Cd or Pb content of original sediment material, before loading.

Further release studies, using natural sediments instead of laboratory-enriched sediments, will add to our knowledge of the nature of heavy metals in Susquehanna River sediments and their potential for release into the aquatic biosphere. (Some additional experiments to determine ion-exchangeable metals are being carried out by doctoral candidate Paul Figura using a chelating resin in the Ca^{2+} form.)

3. Heavy Metal Transport Load, for SRB-NYS and for Entire Susquehanna Basin

The transport of HM's into Pennsylvania by suspended solids from SRB-NYS was calculated as follows: the HM concentrations in sediment from the downstream sites on the Chemung (i.e., sites BF and CH, Table VII) and on the Upper Susquehanna (i.e., sites AP and SB, Table VII) were averaged separately for the two sub-basins, then combined using the available 1:1.8 sediment discharge ratio for the Chemung and Upper Susquehanna sub-basins, respectively (16),* giving weighted-average downstream HM concentrations; these weighted-average concentrations were used with the weighted-average particle-size distribution (III.B.1.a) and the average element concentration ratios in sand/silt/clay (Table XIII) to calculate, as in Appendix A, the average downstream HM concentrations in each size fraction, which are shown in Table XIX. Then from the annual sediment transport load for the SRB-NYS of 1.0 x 10^6 T/yr (16),* and assuming that the suspended load was 10% sand, 55% silt, and

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*Recent sediment data (43) emphasize that this ratio and the total annual discharge are subject to large statistical fluctuations. For the 1975 Water Year the ratio was 1:1 on a total transport of 2.2 x 10^6 T; omitting the discharge in the last week of the water year from Tropical Storm Eloise, the ratio would have been 1:0.66 on a total transport of 1.2 x 10^6 T.

Table XIX. Calculated HM Concentrations in Sand, Silt, and Clay Fractions of Average Downstream Sediment Samples from SRB-NYS and SRB.[a]

Size Fraction	Element Concentrations, µg/g (unless otherwise noted)											
	Ag	As	Cd	Cr	Cu	Fe (mg/g)	Hg	Mn	Ni	Pb	Zn	%C
From SRB-NYS												
Sand	1	.26	1.1	6.4	12	8.2	.032	258	14	18	56	.35
Silt	5	.45	4.8	11.6	41	12.2	.124	412	35	31	107	1.52
Clay	16	3.2	10.3	43	153	37.6	.57	541	109	107	281	2.63
From SRB												
Sand	4	6.7	.83	14	37	10	.02	700	17	201	203	2.86
Silt	23	10.6	3.7	26	125	15	.08	1110	42	342	336	13
Clay	76	80	8.3	97	479	46	.36	1460	131	1190	1020	25

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[a] Method of calculation described in text; Ag calculation assumes zero contribution from Chemung sub-basin, for SRB-NYS concentrations.

35% clay (16), the annual transport load for each element in each size fraction was calculated (Table XX).

Similarly, the calculation for the sediment transport of HM's from the SRB into Chesapeake Bay was based on the element concentration and particle size distribution for samples from three stations near the mouth of the Susquehanna River (24). Since the size distribution was quite variable, calculations of element concentrations in sand, silt, and clay fractions were done separately for each station, then averaged (Table XIX). Then, using the sediment transport load from the Susquehanna River of 2.7×10^6 T/yr and the average size distribution of 10% sand, 50% silt, and 40% clay (16), the transport of HM's in T/yr was calculated (Table XX).

For eight out of twelve elements, the concentrations in downstream sand, silt, and clay fractions are higher for the SRB sediments than for the corresponding SRB-NYS sediments. For As, Cu, Mn, Pb, Zn and %C, the concentrations are 3X or more greater for SRB than for SRB-NYS. The higher arsenic may be due to the fact that the method used for the SRB samples was for total As while a surficial method was used for the SRB-NYS samples. In the case of Hg, the SRB concentrations for total Hg were apparently lower than the surficial SRB-NYS concentrations, although near the limit of detection for Hg in SRB samples (24). Silver and Cr were 2X higher in SRB than in SRB-NYS samples, while Cd, Fe, and Ni concentrations were about the same in the two cases.

The calculated transport of HM's by sediments is shown in Table XX. The annual load of metals transported from the SRB, ranging from 0.5 T/yr for Hg to 69,000 T/yr for Fe, is much greater than from the SRB-NYS,

Table XX. Surficial Heavy Metal Transport by Sediment Material

Size Fraction	Heavy Metal Transport, T/yr									
	Ag	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn
From SRB-NYS											
Sand	0.1	.03	0.1	.6	1.2	800	.003	25	1.4	2	5
Silt	2.7	.24	2.6	6.1	22.	6,600	.067	222	19.	17	58
Clay	5.5	1.0	3.5	14.7	52.	12,900	.19	186	37.	37	96
Total	8.3	1.2	6.2	21.	75.	20,300	.26	433	57.	56	159
From SRB											
Sand	1.2	1.8	.2	3.8	10	2,700	.005	188	4.8	54	55
Silt	34.	16.	5.6	39.	186	22,300	.114	1,650	63.	508	573
Clay	72.	75.	7.8	91.	452	43,900	.35	1,380	124.	1,120	960
Total	107.	93.	13.6	134.	648	68,956	.47	3,222	193.	1,685	1,588

reflecting the higher sediment discharge and in most cases the higher metal concentrations.

The total HM discharge for a river is the sum of the insoluble load (Table XX) and the soluble load, calculated from the average element concentrations in filtered RW and the annual water discharge. Using the soluble loads for SRB-NYS calculated previously (1),* the annual transport load for seven trace metals has been calculated. These loads, and the percentages carried by sand, silt, clay, and dissolved fractions are shown in Table XXI. It is evident that most of the load is carried in solution or by clay particles.† The dissolved load transports 28 to 50% of the total load, the clay fraction carries 28 to 44%, silt carries 13 to 26%, and sand carries only 2% or less. The highest dissolved %'s were for Cd and Hg, and the lowest for Zn.

From the concentrations of Cd and Pb calculated for SRB clay (Table XIX), the dissolved concentrations were estimated using the adsorption isotherms for these metals (Fig. 9a & 9b), yielding the values 0.5 μg/ℓ for Cd and 25 μg/ℓ for Pb. Then, from the average annual SRB discharge of 3×10^{10} m^3, the loads of dissolved Cd and Pb were calculated. The total transport load for Pb (Table XXI) is ∿25X higher from SRB than from SRB-NYS, with a somewhat higher percentage carried by suspended solids. The transport pattern for Cd appears similar for the SRB and SRB-NYS basins.

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[*] i.e., Cd 6.1, Cr 17, Cu 52, Hg 0.26, Ni 44, Pb 52, and Zn 61 T/yr, from average 1974 soluble concentrations of 0.7, 2, 6, 0.03, 5, 6, and 7 μg/ℓ, respectively.

[†] In samples from the Amazon and Yukon rivers, Gibbs reported that only <1 to 17% of the HM's were in the dissolved fraction (43a).

Table XXI. Transport of Trace Metals by Susquehanna River[a]

Element	Total Transport T/yr	Percentage Carried By			
		Sand	Silt	Clay	Dissolved Species
From SRB-NYS, into Pennsylvania					
Cd	12.3	1.	21.	28.	50.
Cr	38.4	2.	16.	38.	44.
Cu	127.	1.	17.	41.	41.
Hg	0.52	1.	13.	36.	50.
Ni	101.	1.	19.	36.	44.
Pb	108.	2.	16.	34.	48.
Zn	220.	2.	26.	44.	28.
From SRB, into Chesapeake Bay					
Cd	29.	1.	20.	27.	52.
Pb	2,430.	2.	21.	46.	31.

[a] Based on 1974-75 concentration data for dissolved and surficial trace metals (14, and this report).

These transport calculations for SRB-NYS are subject to uncertainties (1) in the average HM concentrations in downstream sediments (e.g., the changes in 1975 after Tropical Storm Eloise), (2) in the ratios of HM concentrations in sand, silt, and clay, (3) in the annual water discharge (e.g., the actual discharge for Water Year 1975 was about 20% higher than the long-term average used in the above calculations), (4) in the annual sediment discharge (even more uncertain, based on limited data and varying approximately as the square of the water discharge (44)), (5) in the average distribution of sand, silt, and clay in the sediment discharge, and (6) in the proportions of water and sediment coming from each sub-basin.

River transport is obviously highly dependent on storm events, which can increase the water discharge by an order to magnitude or more, thus increasing dramatically the sediment discharge rate. In the future, using instantaneous water and sediment discharge data, more accurate rate and integral values for the HM transport by water and by sediment can be determined.

In Table XXII the HM discharge from SRB-NYS, in T/yr/1000 km^2, is compared with that from the Rhine River (34), a river comparable in water and sediment discharge per unit area, but "the prototype of a river in which industrial wastes and other pollutants are drained in large quantities (reference 34, p. 6)." Since the Rhine data were based on only the <0.016 mm sediment (∿90% of the <2 mm HM load, according to SRB-NYS data), and the analytical methods gave "total" HM instead of "surficial" HM (see surficial/total ratios, reference 1, p. 18), the data were adjusted to the SRB-NYS basis where possible.

Table XXII. Comparison of HM Discharge by SRB-NYS and by the Rhine R.

Element	SRB-NYS, 1974-75*		Rhine R. Basin, 1970†		Discharge Ratio Rhine/SRB-NYS
	T/yr/1000 km^2	% Soluble	T/yr/1000 km^2	% Soluble	
Ag	0.44 sediment only	--	--	--	--
As	0.06 sediment only	--	6.0	43	--
Cd	0.64	50	1.6 → 1.3‡	69‡	2.0/1
Cr	2.0	44	28 → 14‡	60‡	7/1
Cu	6.7	41	15 → 11‡	49‡	1.6/1
Fe	1,200**	8	--	--	--
Hg	0.028	50	0.65	43	23/1
Mn	44**	48	--	--	--
Ni	5.3	44	6.9 → 6.6‡	80‡	1.2/1
Pb	5.7	48	17.4 → 8.2‡	57‡	1.4/1
Zn	11.6	28	125 → 116‡	67‡	10/1

*SRB-NYS: area 18.9×10^3 km^2; av. water discharge 1.0×10^{10} m^3/yr; sed. discharge 1.0×10^6 T/yr (18).

**Assuming soluble Fe and Mn were 150 and 40 µg/ℓ, respectively (43).

†Rhine Basin: area 145×10^3 km^3; av. water discharge 7.5×10^{10} m^3/yr; sed. discharge (<.016 mm), 3.5×10^6 T/yr (34).

‡ Adjusted to basis of SRB-NYS data (see text).

It is surprising how close the Rhine discharge data are to the SRB-NYS data for Cd, Cu, Ni, and Pb. Evidently the SRB-NYS is nearly as polluted in these elements as was the Rhine Basin in 1970. The Rhine exceeds the SRB-NYS by about an order of magnitude in Cr, Hg, and Zn discharge. Further, the Zn/Cd discharge ratio for the Rhine is 90/1, close to the natural abundance ratio, but for SRB-NYS this ratio is only 18/1, indicating also that Cd pollution here is heavier than Zn pollution. [Three analyses of Binghamton-Johnson City sewage sludge from Mar. '74 to Apr. '75 gave Zn/Cd ratios ranging from 22/1 to 144/1 (14), which does not seem abnormally low, although the normal Zn/Cd ratio for Swedish sludge is ∿200/1 (45).] The adjusted % Soluble was higher in the Rhine than in the SRB-NYS discharge for all elements, especially for Ni and Zn.

As additional data on dissolved and suspended HM's for the entire Susquehanna Basin become available, it will be possible to compare the discharge per unit area for SRB-NYS with SRB. Preliminary comparisons, based on Helz's report (25), indicate approximately equal discharge for Cr, Fe, Mn, Ni, and Zn, but much higher unit area discharge for Cd, Cu, and Pb from SRB-NYS than from the entire SRB.

4. Modeling the HM Transport of a River*

Each river has its own geomorphological features which are dependent on factors such as climate, precipitation, basin size, prevailing geological structures, soil types, and stream profile gradient.

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*Taken from the Master's Thesis of G. J. Hollod (18).

These factors determine the discharge of water and sediment (suspended solids and bed load) in a river, the mineralogy of the sediment and its particle-size distribution.

The particle size distribution of bottom sediment will vary considerably from river to river and from station to station in a given river. The variations in size distribution of bottom sediment are related to the velocity of the water. Thus a bottom sediment sample taken in the shallow riffle area of a river will have sediment particles which will be mostly sand size or large silt material, while in slower moving water in pool areas of a river the bottom material will be richer in clay and fine silt.

Clay and fine silt-size particles generally make up the suspended load and move essentially as part of the stream flow, since the particles are maintained in suspension by the upward components of turbulent flow or by colloidal suspension. The sand and the larger silt particles, on the other hand, make up most of the bed load and the discharge of the bed load material is closely related to the size of the bed materials and to stream hydraulics. Generally, the total bed load is much less than the total suspended load.

To a first approximation, the sediment discharge of a river, S, is exponentially related to the water discharge, Q by the equation

$$S = kQ^n$$

where k is a constant and n has a value ranging from 1.5 to 2.5 for many river basins (44). During high flow periods, the water discharge is higher and so is the concentration of suspended solids; since both of these quantities are multiplied to give S, the exponential relationship is understandable. Recent sediment discharge data indicate that $n \cong 2$ for SRB-NYS (43).

Schubel has shown that 70% of the annual discharge of sediment material into Chesapeake Bay from the Susquehanna River occurs normally in less than a two month period between February and March (46). During Tropical Storm Agnes in June 1972 the suspended load reached ∿10,000 mg/ℓ, probably from the scouring out of upstream impoundments, and discharged in a one-week period a supply of suspended solids exceeding that of the past several decades (47).

Such storm events, responsible for most of the HM transport by a river, cannot be predicted with any statistical reliability, but given the discharge data it may be possible to calculate the HM transport.

The prediction of a pollutant's mobility is based on the continuous interactions that the pollutant has within the hydrologic cycle. The simultation and prediction of processes originating from pervious or impervious lands, from agricultural or urban areas, from natural or developed lands, the major transport modes of runoff and sediment loss, and the chemical interaction of the pollutant with soil and water must all be considered when trying to simulate accurately a natural transport model. An early general hydrologic computer model was developed by Crawford for non-point source pollution in the Stanford Watershed in California (48), and this was followed by a model dealing more with fluvial processes called the Wisconsin Hydrologic Transport Model WHTM (49). Recently, workers at the Oak Ridge National

Laboratory have developed a Unified Transport Model which combines the land simulating transport processes of the Stanford Watershed Model with the hydrologic transport processes of the WHTM (50).

Fields (51) developed a model (CHNSED) for sediment and trace contaminant transport which merges WHTM with a model for suspended and bed load transport and composition (SEDTRN). He successfully correlated particle size distribution of suspended sediment and bed sediment in the Rio Grande River. With this model, the total discharge of sediment material as a function of mean water flow velocity could be predicted. Patterson et al. applied the Unified Transport Model (UTM) with an interdisciplinary team to the Crooked Creek Watershed of the New Lead Belt in Southeast Missouri to estimate atmospheric and hydrologic transport rates and environmental concentrations of lead in the vicinity of a lead smelter (52). From their results, they concluded that the accuracy of the UTM for predicting lead budgets in this area was dependent on the amount of experimental data available for optimizing certain parameters in the UTM.

Raridon et al. recently modeled successfully the discharge of K^+ and Cd^{2+} for the Walker Branch Watershed in Tennessee, using data which had been collected in the watershed for 6 years to optimize the parameters of the model (53).

Lassiter (54) reported on a predictive model for the behavior of mercury in the aquatic environment. His attempt emphasized the difficulties in determining partition coefficients between mercury species and undefined natural suspended materials, and much uncertainty arose because of multi-parameter interactions within the aquatic system (e.g., pH, salinity, and organic complex formation).

In spite of such difficulties, order of magnitude calculations can be made from adequate discharge data and chemical analyses of representative water and sediment samples, as shown in this report. Further study will show whether the HM concentration ratios in sand/silt/clay are reasonably constant from region to region in the Susquehanna Basin; if they are not constant, additional data may establish the relative significance of pollution and geochemical background in determining these ratios.

IV. CONCLUSIONS

This study presents additional data on the characterization and analysis of bottom sediment samples from the SRB-NYS. The analytical results help establish baseline values for the surficial concentrations of eleven heavy metals (Ag, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn) and the total organic C in sediments.

The data indicate that sediment analyses can be used to demonstrate HM pollution in rivers more effectively than by water monitoring.

Intensive sampling downstream from Binghamton showed pollution profiles for Ag,Cd,Cu & Hg with values approaching baseline concentrations at increasing distances downstream. The profiles for Ag and Cd were highly correlated.

Tropical Storm Eloise significantly lowered the concentrations of most trace metals in the sediments downstream from the Binghamton urban area, showing the tendency of high water to scour the channel.

The source of high Ni and Zn in Tioga Basin sediments was traced to acid mine drainage from the Blossburg, PA. area.

For most elements, there is a general increase in concentration with decreasing particle size. For each trace metal, the concentration ratio in sand/silt/clay was relatively constant, even after Eloise which changed the absolute concentrations markedly. The HM concentration ratios tended to be higher than the CEC ratios for sand/silt/clay, especially for elements shown to be pollutants.

Average downstream bottom sediments consisted of 76% sand*, 23% silt, and 1% clay. Mineralogical studies showed the sand fraction to be mainly quartz, sandstone, siltstone, shale, and feldspar. The clay fraction contained illite and chlorite in approximately a 6:4 ratio. The samples had ∿1% oxidizable organic C, of which only 5% was represented by extractable humic and fulvic acids. However, these humic substances could have accounted for ∿20% of the observed CEC of the various size fractions.

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*USGS basis

Statistical analysis of the results on many samples, analyzed as separate size fractions, showed that element-element correlations among size fractions of an individual sample were stronger than correlations for different samples within a given size fraction. Few significant element-element correlations with C, Fe, or Mn were noted, but correlations among the "pollution" elements Ag, Cd, Cu, Ni, and Zn were common. A study of the degree of extraction of various HM's with selective leaching media may help elucidate the mechanism of binding and transport of the HM's, and thus clarify the observed extent of correlations.

As a further aid in understanding the mechanism of HM transport, studies on the uptake and release of Cd(II) and Pb(II) by sediment materials are reported. These materials were very effective in taking up Cd and Pb at low solution concentrations from a river water medium, and data on river samples taken after storms correlated roughly with the in vitro adsorption studies. Also, the release of Cd and Pb from loaded sediments into various media has interesting environmental implications.

The annual sediment transport load for HM's from the SRB-NYS, ranging from 0.26 T/yr for Hg to 20,300 T/yr for Fe, is much lower than for the entire SRB, reflecting the lower sediment discharge and in many cases the lower metal concentrations of the sediments. Nevertheless, on a unit area basis, the discharge of HM's from the SRB-NYS is significant, approaching for several metals the discharge per unit area of the Rhine River!

Comparisons of the present results with data from other river systems show many similarities.

REFERENCES

1. B. McDuffie, "Preliminary Study of Sediments from the Susquehanna River Basin in New York, with Emphasis on Surficial Heavy Metal Content," Susquehanna River Basin Commission, Mechanicsburg, PA, June 1975.
2. H. P. Guy, "Techniques of Water-Resources Investigation, Book 5, Chap. C1, Laboratory Theory and Methods for Sediment Analysis," U.S. Geol. Surv., U.S. Dept. Interior, Washington, D.C., 1969.
3. W. C. Krumbein, Size frequency distribution of sediments, J. Sed. Petrology, 36, 811 (1934).
4. W. C. Krumbein and F. J. Pettijohn "Manual of Sedimentary Petrography," D. Appleton Century Co., New York, 1938.
5. G. Brown, "The X-Ray Identification and Crystal Structures of Clay Minerals," Mineralog. Soc., London, 1961, p. 544.
6. M. L. Jackson, Frequency distribution of clay minerals in major great soil groups as related to factors of soil formation, in Clays and Clay Minerals, 6th Proc. Nat. Conf. Clays and Clay Minerals, New York, Pergamon Press, 1959, p. 133.
7. T. Tamura, Identification of the 14 Å clay mineral component, Amer. Mineral, 42, 107 (1957).
8. H. P. Klug and L. E. Alexander, "X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials," 2nd ed., Wiley, New York, 1974.
9. L. G. Schultz, Quantitative X-ray determinations of some aluminous clay minerals in rocks, in Clays and Clay Minerals, 7th Proc. Nat. Conf. Clays and Clay Minerals, Pergamon Press, New York, 1960, p. 216.

10. R. L. Malcolm and V. C. Kennedy, Variation of cation-exchange capacity and rate with particle size in stream sediment, J. Water Pollut. Control Fed., 42, R153 (1970).

11. B. Malo, USGS provisional procedure for sediment analysis, U.S. Geol. Surv. Laboratory, Albany, N.Y. (personal communication, 1974).

12. W. R. Hatch and W. L. Ott, Determination of sub-microgram quantities of mercury by atomic absorption spectrophotometry, Anal. Chem., 40, 2085 (1968).

13. M. L. Jackson, "Soil Chemical Analysis," Prentice-Hall, Englewood Cliffs, New Jersey, 1958, p. 57.

14. I. A. El-Barbary, "Trace Metals in Upper Susquehanna River Ecosystem: Environmental Distribution, Urban Impacts, and Interaction with Sediment Materials," Ph.D. Thesis, State University of New York at Binghamton, Binghamton, N.Y., 1976.

15. "Binghamton Waste Water Management Study Phase II: Waste Water Management Alternatives," Lawler, Matusky, and Skelly Engineers, Tappan, N.Y., March 1974, p. III-22.

16. K. F. Williams and L. A. Reed, Stream sedimentation in the Susquehanna River Basin, hydrologic effects of land use, U.S. Geol. Surv., Water-Supply Pap. 1532-F, 1972.

17. D. Carrol, Ion exchange in clays and other minerals, Geol. Soc. Amer. Bull., 70, 749 (1959).

18. G. J. Hollod, "Characterization of Bottom Sediments from the Susquehanna River Basin in New York State, with Emphasis on Surficial Heavy Metal Concentrations and Transport," M.A. Thesis, State University of New York at Binghamton, Binghamton, N.Y., 1976.

19. H. E. Hawkes and J. S. Webb, "Geochemistry in Mineral Exploration," Harper and Row, New York, 1962, p. 166.

20. B. G. Oliver, Heavy metal levels of Ottawa and Rideau River sediments, Environ. Sci. Technol., 7, 135 (1973).

21. V. C. Kennedy, Mineralogy and cation-exchange capacity of sediments from selected streams, U.S. Geol. Surv., Prof. Pap. 433-D, Washington, D.C., 1965.

22. R. W. Lahann, The effect of trace metal extraction procedures on clay minerals, J. Environ. Sci. Health, in press, 1976.

23. M. Schnitzer and S. U. Khan, "Humic Substances in the Environment," Marcel Dekker, Inc., New York, 1972.

24. J. R. Hollowell, "Results of Initial Sampling of Heavy Metals and Pesticides found in Stream Bottom Sediments in the Susquehanna River Basin," Susquehanna River Basin Commission, Mechanicsburg, Pennsylvania, Nov. 1975.

25. G. R. Helz, Trace element inventory for the northern Chesapeake Bay with emphasis on the influence of man, Geochim. Cosmochim. Acta, 40, 573 (1976).

26. B. G. Oliver and H. Agemian, "Further Studies on the Heavy Metal Levels in Ottawa and Rideau River Sediments," Inland Waters Dir., Water Quality Branch, Ottawa, Can., Scientific Ser. No. 37, 1974.

26a. B. G. Oliver and J. Kinrade, "Heavy Metal Concentrations in Ottawa River and Rideau River Sediments," Inland Waters-Branch, Dept. of the Environ., Ottawa, Can., Scientific Ser. No. 14, 1972.

27. D. P. Proctor, T. Butz, and B. Sinha, Heavy metal additions to the surface waters, stream sediments and selected aquatic life in the Meramec Park Reservoir Drainage Basin, Proc. of the 10th Annual Conf. on Trace Substances in Environmental Health, D. D. Hemphill (ed.), Univ. Missouri, Columbia, Mo., 1976.

28. C. Colinson and N.F. Shimp, Trace elements in bottom sediments from Upper Peoria Lake, Middle Illinois River: a pilot project, Environ. Geol. Note 34, Ill. State Geol. Surv., 1973.

29. R. H. Carpenter, T. A. Pope, and R. L. Smith, Fe-Mn oxide coatings in stream sediment geochemical surveys, J. Geochem. Explor., 4, 349 (1975).

30. J. Kronfeld and J. Navrot, Aspects of trace metal contamination in the coastal rivers of Israel, Water, Air, and Soil Pollut., 4, 127 (1975).

31. S. C. Harding and H. S. Brown, Distribution of selected trace elements in sediments of Pamilico River Estuary, North Carolina, Environ. Geol., 1, 181 (1976).

32. G. Muller and U. Förstner, Heavy metals in sediments of the Rhine and Elbe estuaries: mobilization or mixing effect?, Environ. Geol., 1, 33 (1975).

33. J. Kubota, E. L. Mills, and R. T. Oglesby, Lead, Cd, Zn, Cu, and Co in streams and lake waters of Cayuga Lake Basin, New York, Environ. Sci. Technol., 8, 243 (1974).

34. A. J. de Groot and E. Allersma, Field observations on the transport of heavy metals in sediments, Conf. on Heavy Metals in the Aquatic Environment, Peter A. Krenkel et al.(ed.), Vanderbilt Univ., Nashville, Tenn., Dec. 1973.

35. "Soil Survey: Broome County, New York," U.S. Dept. of Agriculture Soil Conservation Service, in Cooperation with Cornell University Agricultural Experiment Station, U.S. Govt. Printing Off., Washington, D.C., March 1971.

36. M. T. El-Ashry, Trace elements in Pennsylvania shales in relation to environmental health in Northeastern Pennsylvania, Geol. Soc. Amer. Bull., 82, 1425 (1971).

37. B. Mason, "Principles of Geochemistry," John Wiley and Sons, Inc., New York, 1966, p. 180.

38. R. E. Pitt and G. Amy, Toxic Materials Analysis of Street Surface Contaminants, EPA Technology Series, Report EPA-R2-73-283, Environmental Protection Agency, Washington, D.C., August 1973.

39. J. Gardiner, The chemistry of cadmium in natural waters, II. The adsorption of cadmium on river nuds and naturally occurring solids, Water Res. 8, 157 (1974).

40. J. Vuceta, "Adsorption of Pb(II) and Cu(II) on α-Quartz from Aqueous Solutions: Influence of pH, Ionic Strength, and Complexing Ligands," Ph.D. Thesis, Calif. Inst. of Tech., Pasadena, 1976.

41. B. McDuffie, I. El-Barbary, G. J. Hollod, and R. D. Tiberio, Trace metals in rivers--speciation, transport, and role of sediments, Proc. of the 10th Annual Conf. on Trace Substances in Environmental Health, D. D. Hemphill (ed.), Univ. Missouri, Columbia, MO, 1976.

42. R. S. Reimers and P. A. Krenkel, Kinetics of mercury adsorption and desorption in sediments, J. Water Pollut. Control. Fed. 46, 352 (1974).

43. "Water Resources Data for New York, Water Year 1975," U.S. Geol. Surv. Water-Data Report NY-75-1, prepared in cooperation with the State of New York and with other agencies, U.S. Geol. Surv., Water Resources Div., P.O. Box 1350, Albany, N.Y. 12201.

43a. R. J. Gibbs, Mechanisms of trace metal transport in rivers, Science, 180, 71 (1973).

44. L. B. Leopold, M. G. Wolman, and J. P. Miller, "Fluvial Processes in Geomorphology," Academic Press, San Francisco, 1964, p. 238.

45. V. Tullander, Final disposal of municipal sludge in Sweden, J. Water Pollut. Control Fed. 47 (4), 688 (1975).

46. J. R. Schubel, Distribution and transportation of suspended sediment in Upper Chesapeake Bay, Geol. Soc. Amer. Mem. 33, 151 (1972).

47. J. R. Schubel, Effects of Tropical Storm Agnes on the suspended solids of the northern Chesapeake Bay, in "Suspended Solids in Water," R. J. Gibbs (ed.), Plenum Press, 1974.

48. N. H. Crawford and K. K. Linsley, "Digital Simulation in Hydrology: Stanford Watershed Model IV," Dept. of Civil Engineering, Stanford Univ., Tech. Rept. No. 39, Stanford, CA, 1966.

49. M. R. Patterson, J. K. Munro, D. E. Fields, R. D. Ellison, A. A. Brooks, and D. D. Huff, "A User's Manual for the Fortran IV Version of the Wisconsin Hydrologic Transport Model," ORNL/NSF/EATC-7, Oak Ridge National Laboratory, 1974.

50. W. Fulkerson, W. D. Shults, and R. I. Van Hook, (eds.), "Ecology and Analysis of Trace Contaminants Progress Report, June 1972-January 1973", ORNL/NSF/EATC-1, Oak Ridge National Laboratory, March 1973.

51. D. E. Fields, "CHNSED: A Model of Sediment Transport in Streams," ORNL/NSF/EATC-19, Oak Ridge National Laboratory, March 1976.

52. M. R. Patterson, J. K. Munro, R. J. Luxmore, Simulation of lead transport on the Crooked Creek Watershed, Proc. of the 9th Annual Conf. on Trace Substances in Environmental Health, D. D. Hemphill (ed.), Univ. Missouri, Columbia, MO, 1975.

53. R. J. Raridon, D. E. Fields, and G. S. Henderson, "Hydrologic and Chemical Budgets on Walker Branch Watershed: Observations and Modeling Applications," ORNL/NSF/EATC-24, Oak Ridge National Laboratory, 1976.

54. R. R. Lassiter, G. L. Baughman, J. L. Malanchuk, Predictive modeling of the behavior of pollutants in the aquatic environment, Symp. on Nonbiological Transport and Transformation of Pollutants on Land and Water: Processes and Critical Data Required for Predictive Description, National Bureau of Standards, Gaithersburg, Md, May 1976.

55. R. M. Perhac, Distribution of Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn in dissolved and particulate solids from two streams in Tennessee, J. Hydrol., 15, 177 (1972).

56. P. R. Whitney, Relationships of manganese-iron oxide associated heavy metals to grain size in stream sediments, J. Geochem. Explor. 4, 251 (1975).

APPENDIX A

CALCULATION OF ELEMENT CONCENTRATION IN SEPARATE SIZE FRACTIONS FROM WHOLE SAMPLE DATA AND SAND/SILT/CLAY RATIOS

Definitions:

f_{sa} = fraction of sand in sample
f_{si} = fraction of silt in sample
f_{cl} = fraction of clay in sample

C_{sed} = overall concentration of element in unfractionated sediment sample

C_{sa} = concentration of element in sand
C_{si} = concentration of element in silt
C_{cl} = concentration of element in clay

$r_{si} = C_{si}/C_{sa}$ (i.e., the average ratio) (A-1)
$r_{cl} = C_{cl}/C_{sa}$ (i.e., the average ratio) (A-2)

It follows that

$$C_{sed} = f_{sa} \cdot C_{sa} + f_{si} \cdot C_{si} + f_{cl} \cdot C_{cl} \qquad \text{(A-3)}$$

Assuming that the average ratios, r_{si} and r_{cl}, apply to the sample in question

from Equation A-1: $C_{si} = r_{si} \cdot C_{sa}$ (A-4)

and

from Equation A-2: $C_{cl} = r_{cl} \cdot C_{sa}$ (A-5)

Substituting in Equation A-3:

$$C_{sed} = f_{sa} \cdot C_{sa} + f_{si} \cdot r_{si} \cdot C_{sa} + f_{cl} \cdot r_{cl} \cdot C_{sa} \qquad \text{(A-6)}$$

Collecting terms and rearranging:

$$C_{sa} = \frac{C_{sed}}{f_{sa} + f_{si} \cdot r_{si} + f_{cl} \cdot r_{cl}} \qquad \text{(A-7)}$$

C_{si} and C_{cl} can then be calculated from A-4 and A-5.

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